PB-217 786

CHEMICAL ASPECTS OF H_2S REMOVAL IN SOIL

Robert Clark Gumerman

Washington University
Seattle, Washington

1968

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

CHEMICAL ASPECTS OF H_2S REMOVAL IN SOIL

by

ROBERT CLARK GUMERMAN

A thesis submitted in partial fulfillment

of the requirements for the degree of

DOCTOR OF PHILOSOPHY

UNIVERSITY OF WASHINGTON

1968

Approved by_____
(Chairman of Supervisory Committee)

Department_____
(Departmental Faculty Sponsoring Candidate)

Date_____

Chemical Aspects of H_2S Removal in Soil

by Robert Clark Gunerman

Chairman of Supervisory Committee: Professor Dale A. Carlson

Department of Civil Engineering

Recent applications of the relatively new soil treatment process for the elimination of gaseous malodors emanating from water quality control operations have been very successful. Although past research has indicated that biological organisms were responsible for the oxidation of noxious gases in moist soils, new research indicates that dry, sterile soil can remove H_2S, one of the more common gases released by septic sewage. This study was directed toward an investigation of the chemical aspects of H_2S removal by both moist and dry sterile soils. Batch scale tests were utilized to study the effect of temperature on removal efficiency, the ability of a soil to be rejunenated, the desirability of certain common cations in the soil, and selection of an easily measured soil property or characteristic which relates the H_2S removal capacity of different soils. The principal objectives of dynamic testing included a study of the effect of soil temperature and moisture on removal efficiency, and the determination of a method of design optimization.

The H_2S removal mechanism by dry, sterile soil may be best described as contact catalysis, two distinct reactions comprising the mechanism. Initially, H_2S reacts with a heavy metal oxide, denoted by MO_x, according to the reaction

$$MO_x + xH_2S \longrightarrow MS_x + xH_2O$$

The heavy metals most desirable at the soil surface include Cu^{+2}, Fe^{+3}, Zn^{+2}, and Ni^{+2}. In the presence of air or oxygen, the metal-sulfide complex MS_x is oxidized to produce the initial cation oxide, according to the reation

$$2MS_x + XO_2 \longrightarrow 2MO_x + \text{SULFUR}$$

Although these two reactions occur concurrently, at an H_2S concentration of 10% the initial reaction rate exceeded the rate of rejuvenation, necessitating an additional rejuvenation period when only air was allowed to contact the soil. At this 10% concentration, one cubic foot of sterile, dry loam soil can remove up to 1.11 pounds of H_2S.

During passage of H_2S through soil, the reaction zone temperature and detention time determine the "service time" prior to breakthrough. Although the removal mechanism is exothermic, increasing the reaction temperature results in a more rapid removal rate and therefore more efficient utilization of the soil. Such increases in reaction temperature may be achieved by increasing the inflow temperature or the amount of H_2S entering. However, increasing reaction temperature by increasing total flow also decreases detention time. At H_2S concentrations of 10%, detention times of six minutes are adequate; however, it is logical that lower detention times would suffice at lower concentrations.

A method of design optimization has been developed based upon selection of the total flow rate per square foot of surface, for a given soil depth, which provides the maximum H_2S removal prior to breakthrough. Utilizing this method of optimization should prove of great benefit in the further application of this process to water quality control operations emanating gaseous malodors.

TABLE OF CONTENTS

		Page
I	Introduction	1
	A. The Problem	2
	B. Purpose and Scope	4
II	Previous Work	5
III	Theoretical Considerations	13
	A. Adsorption	14
	B. Water Solution	19
	C. Ion Exchange	20
	D. Contact Catalysis	23
	E. Summary	25
IV	Experimental Methods	26
	A. Apparatus Used	27
	B. Experimental Techniques	28
V	Results	33
	A. Liquid-Soil Batch Uptake Tests	34
	B. Gas-Soil Batch Uptake Tests	44
	C. Surface Area Measurements	52
	D. EDTA Removal from Solution	52
	E. Dynamic Uptake of Hydrogen Sulfide from Air Streams	53
VI	Discussion	60
	A. Influence of Moisture upon the Removal Mechanism in Batch Scale Testing	61
	B. Influence of Moisture upon Dynamic Removal Situations	64
	C. Soil Rejuvenation in Dry Dynamic Removal Situations	64

TABLE OF CONTENTS (Continued)

		Page
	D. Removal of Sulfide from Liquid-Soil Systems	67
	E. Hydrogen Sulfide Removal in Static Gas-Soil Systems	72
	F. The Suggested Method of Design Optimization	76
VII	Summary	81
VIII	References	84
IX	Appendices	87
	A. Henry's Law Constants for Hydrogen Sulfide in Distilled Water	88
	B. Example Calculation of Hydrogen Sulfide Solubility in Distilled Water	89
	C. Composition of Buffer Mixtures	90
	D. Effective Ionic Radii of Selected Cations	91
	E. Calculations for Breakthrough Time Assuming No Interaction Between Hydrogen Sulfide and the Soil	92
	F. Liquid-Soil Batch Uptake Data	94
	G. Gas-Soil Batch Uptake Data	100
	H. Gas-Soil Dynamic Uptake Data	104
	I. Physical Description of Lynden Loam	105
	J. Reaction Zone Temperatures in Dynamic Uptake Tests	106
	K. Future Work	107

LIST OF TABLES

Tables		Page
I	Mercer Island Soil Filter Design Specifications	8
II	Characteristics of Physical Adsorption and Chemisorption	17
III	Calculated Minimum Solubility of Hydrogen Sulfide in Distilled Water	21
IV	Soil Surface Areas	52
V	EDTA Uptake by Various Soils	53
VI	Breakthrough Times, Observed and Calculated, for a 10% H_2S Concentration	65
VII	Summary of Soil Properties in Liquid-Soil Systems . . .	69
VIII	Summary of Soil Properties in Gas-Soil Systems	73

LIST OF FIGURES

Figure		Page
1.	Pomeroy's Diffusion Trench	7
2.	pH Influence on Sulfide Uptake in Liquid-Soil Systems	35
3.	Temperature Influence on Sulfide Uptake in Liquid-Soil Systems	36
4.	Sieve Size Influence on Sulfide Uptake in Liquid-Soil Systems	37
5 - 6	Cation Influence on Sulfide Uptake in Liquid-Soil Systems	38,39
7.	Sulfide Uptake by Several Soils in Liquid-Soil Systems	41
8.	Freundlich Isotherm Plots for Liquid-Soil Systems . .	42
9.	Langmuir Isotherm Plots for Liquid-Soil Systems . . .	43
10.	Temperature Influence on Hydrogen Sulfide Removal in Gas-Soil Systems	45
11.	Sieve Size Influence on Hydrogen Sulfide Removal in Gas-Soil Systems	46
12.	Freundlich Isotherm Plots of Gas-Soil Systems	47
13.	Langmuir Isotherm Plots for Gas-Soil Systems	48
14 - 15	Cation Influence on Hydrogen Sulfide Removal in Gas-Soil Systems	49,50
16.	Hydrogen Sulfide Removal Isotherms for Several Soils in Gas-Soil Systems	51
17.	H_2S Breakthrough Time versus Total Flow at a Constant H_2S Flow Rate	54
18.	H_2S Breakthrough Time versus Total Flow at Fixed H_2S Concentrations	55
19.	H_2S Breakthrough Time versus Number of Rejuvenations.	57
20.	Effect of Influent Temperature on Initial Breakthrough Time	58

LIST OF FIGURES (Continued)

Figure		Page
21.	Soil Moisture Content Influence on Initial H_2S Breakthrough Time	59
22.	Calculated Curves for Solution pH Influence upon Sulfur Species Present	62
23.	Method of Design Optimization	80

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation and thanks to Dr. Dale A. Carlson for the constant encouragement and help which he offered throughout the author's period of graduate study.

A note of appreciation is also extended to Professor Robert O. Sylvester, Dr. Russell F. Christman, and Professor Robert G. Hennes for their efforts involving planning of the research effort and final manuscript preparation.

To Miss Penny Morris, for her help in the laboratory and for typing portions of the manuscript, the author gives extreme thanks.

The author thanks Dr. David D. Wooldridge for analyzing the chemical composition of the soils studied.

For financial aid, the author thanks the United State Public Health Service for funds which were administered by Dr. A. T. Rossano and the Federal Water Pollution Control Administration Research Grant WP 00883 under the direction of Dr. Dale A. Carlson.

I. INTRODUCTION

A. The Problem

Since prehistoric times, man's industrial and domestic activities have been a source of air pollution. Until recently, the odor aspect of this air pollution problem has been generally neglected because it normally created only a nuisance affect and not a health problem. With the current trend of industrialization changing man's living pattern from rural to urban, many odor sources suddenly are adjacent to population centers. This rapid rate of industrialization and urbanization has created many new odor sources, including occasionally odorous sewers and sewage treatment plants, both of which are usually in the vicinity of residential neighborhoods.

Two problems co-exist in the elimination of gaseous malodors. First, they must be collected at the source and second, they must be eliminated. This research concerns itself only with the latter aspect and only for gaseous hydrogen sulfide. Hydrogen slufide was chosen for five reasons. (a) It is one of the most common odorous gases, emanating from many industrial processes and also from septic sewage. (b) Hydrogen sulfide exerts both a health affect and a nuisance affect on humans. Prolonged exposure of the eyes and respiratory tract causes dizziness, nausea, gastrointestinal disturbances, coughing, and dryness in the nose, throat, and chest (1). Higher concentrations can be fatal. (c) By presently used methods, hydrogen sulfide is very difficult and expensive to remove from air streams. (d) In addition to the lowering of property values originating from the nuisance effect, hydrogen sulfide also has the ability to darken lead based paint and destroy certain forms of vegetation. (e) Hydrogen sulfide is readily obtainable for study.

Many methods have been proposed for removing hydrogen sulfide from air streams. These include adsorption on activated carbon, scrubbing with water or chemical solutions, flame combustion using specially designed furnaces, reaction with heavy metals, catalytic combustion units operating at high temperatures and gas concentrations, oxidation with ozone, and masking with a non-nuisance gas (2). In most installations using these principles, the process either does not provide satisfactory removal, is extremely costly to operate, or creates more noxious compounds than hydrogen sulfide.

One of the newer methods for removing hydrogen sulfide consists of passing the laden air stream through beds of soil (3). Pomeroy states that soil microbes are the responsible degradation mechanism in the soil, but current research by the author (4) preliminary to that reported in this dissertation has shown that chemical removal mechanisms predominate at hydrogen sulfide concentrations greater than 700 ppm expressed on a volume basis. This is not to imply that 700 ppm, a concentration higher than normally encountered in sanitary engineering practice, is a lower limit for chemcial removal. Not only is the mechanism unclear, but the capacity of soil to remove hydrogen sulfide and the comparative removal ability of different soils are unknown.

B. Purpose and Scope

Previous laboratory and field scale studies have shown that soil prossesses the ability to remove hydrogen sulfide from air streams. Removal has been interpreted at low hydrogen sulfide concentrations as utilization by soil microbes, but this mechanism has not been verified for hydrogen sulfide concentrations greater than 700 ppm, expressed on a volume basis.

A primary phase of this research was the elucidation of the chemical removal machanism(s) at high hydrogen sulfide concentrations and the influence of parameters such as temperature, hydrogen sulfide concentration, soil pH, soil moisture, and soil surface area upon such mechanisms. Experimental verification is presented for two distinct mechanisms of hydrogen sulfide removal by sterile soil, one mechanism in a liquid-soil system and one in a gas-soil system.

Dynamic testing of the primary test soil was undertaken to determine the maximum capacity of this sterile soil for removal of hydrogen sulfide and the time until initial breakthrough of the hydrogen sulfide as influenced by total mixture flow, concentration of hydrogen sulfide, temperature, and soil moisture. The capacity of sterile soil to self rejuvenate after initial breakthrough was studied under dynamic conditions.

In addition to the Lynden loam which served as the primary test soil, the capacity of sterile samples of a clay, a sand, and a humic soil to remove hydrogen sulfide under static conditions has also been explored. Correlations were sought between sterile fractions of these soils and Lynden loam for both batch gas-solid and batch liquid-solid removals on the basis of surface area, the ability to remove EDTA from buffered liquid solutions, and the chemical composition of the soils.

II. PREVIOUS WORK

Reference to the principle of deodorization of air streams by their passage through soil beds was first mentioned by Pomeroy in 1957 (3). Pomeroy claimed that by passing air laden with sewage odors through a gas permeable soil bed, the odors were removed as a direct consequence of their oxidation by biological growths. Pomeroy felt that the oxidation of the sulfur gases in sewer odors could eventually create a sulfuric acid buildup in the soil, but if the gas flow remained low enough, the alkaline material in the soil and the leaching caused by rainfall and irrigation would never allow a harmful amount of acid to accumulate. As the removal mechanism was felt to be biological, suggestions were made that the soil bed should remain moist at all times.

Pomeroy tested this hypothesis in both laboratory and field scale tests. In the laboratory, an air stream containing iso-valeric acid, skatole, and phenol was passed through a column of moist clay soil, two inches in diameter, by two feet in length. No odor was detectable at the column exit, but according to Pomeroy, "Because of the exploratory nature of this test, no quantitative measurements were made." (3).

The field scale tests were conducted at a sewage pump station in Long Beach, California. Figure 1 illustrates one of the two identical diffusion trenches which were used in the study, total gas flow through the system being maintained at 730 cubic feet per minute. No odors were detected emerging, after the odor of the straw mat placed over the distributing pipes ceased, but no mentioned was made concerning changes in biological population (3).

The next recorded field scale studies were conducted using odors created in sewage wet wells on Mercer Island, Washington in 1962 (5). Whereas Pomeroy's field studies were conducted by pumping the sewer

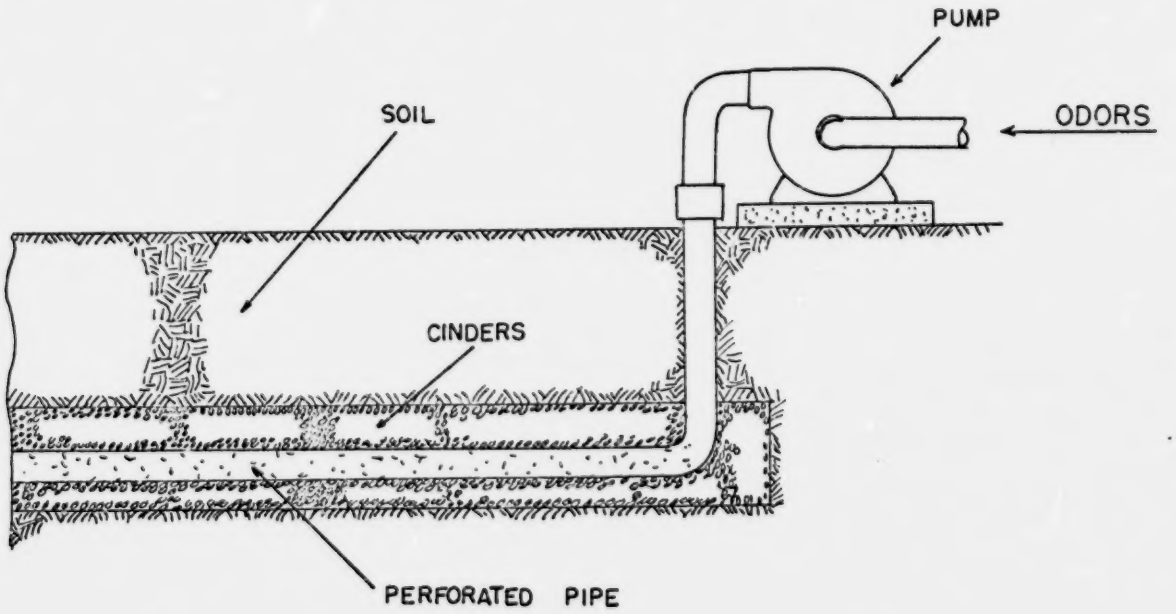


FIGURE 1 - POMEROY'S DIFFUSION TRENCH

gases through the soil, in the Mercer Island installations the gases were forced out of the air tight wet well by the rising sewage level and then through a bed of soil. When the sewage reached the level where the pumps began operating, some of the gases previously expelled along with some air in the soil interstices were drawn back into the wet well. In other words, a breathing action was occurring which resulted in a much longer residence time than if the gases were simply pumped through the soil bed. Design of the soil beds was based upon four inch diameter plastic distribution pipes covered by two inches of gravel and eighteen inches of soil, the ground surface area being determined by the sewage flow through the wet well. Table I indicates what surface areas were felt to be desirable for specified sewage flows.

Table I: MERCER ISLAND SOIL FILTER DESIGN SPECIFICATIONS (5).

Flow	Ground Level Surface Area	Perforated Pipe Length
Under 800 gpm	25 ft^2	1-10 ft. Pipe
800-1800 gpm	50 ft^2	2-10 ft. Pipes
1800-2500 gpm	100 ft^2	4-10 ft. Pipes

Following the installation and successful operation of the Mercer Island soil bed, Leiser (6, 7) conducted a laboratory study to determine the optimum gas flow rates, optimum soil depths, most suitable soils, soil lifetime, and a verification of the removal mechanism. Six inch diameter columns of soil, two and one half feet were used in testing a gas stream flowing at 0.35 cfm/ft^2 of surface area and a hydrogen sulfide concentration of 15 ppm. This amounts to an inflow of 39.1 milliliters S.T.P. of hydrogen sulfide per day or 59.2 milligrams of hydrogen sulfide per day. Conclusions

of the study were that the removal was by soil microbes living in the moist soil, a three month test period did not diminish the 100% removal experienced, and that optimum flow rates would have to be based upon the total concentration of malodors in the gas stream and not simply on a hydrogen sulfide concentration. For the particular flow conditions chosen, a depth of two to two and one half feet was felt to be optimum depth, although it was recognized that other flow rates and concentrations would probably necessitate other depths and/or ground level areas. The moist loam soil studied performed longer and more efficiently than dry loam, clay, or sand columns under similar conditions.

Prior to preparation of this dissertation, the author conducted preliminary research concerning the significance of biological utilization at a hydrogen sulfide concentration of 700 ppm (4). Two columns of soil six inches in diameter and three and one half feet deep were prepared. One of these columns served as a control with only air passing through it, while the test column had an air-hydrogen sulfide mixture passing through it. The testing was conducted over a twelve week period. Total gas flow was two liters per minute (0.36 cfm/ft^2 of surface area) and hydrogen sulfide flow was 1.4 milliliters S.T.P. per minute or 1.97 milligrams of hydrogen sulfide per minute. Detention time was approximately five minutes. Results established in this exploration are listed following:

1. In the test column, the population of bacteria grown on Thiobacillus specific media experienced an initial stimulation in the first five weeks, followed by a decline to the original population after seven more weeks. The control column indicated a steady increase of bacteria grown upon

this same media and at termination the number was approximately double that in the soil having contact with hydrogen sulfide.

2. No significant changes occurred to populations grown upon heterotrophic or fungal specific media in either column.
3. During the twelve weeks, soil elemental sulfur increased to 0.02 grams per gram of soil at the three inch level and soil sulfate increased to 0.017 grams per gram of soil at this same level. Lesser amounts of elemental sulfur and sulfate were found at higher levels. No sulfur balance could be attempted due to a system leak.
4. In the test column, soil pH decreased continually to a low of pH 3.4, while dropping only slightly in the control column.
5. The removal efficiency of the lower soil layers became progressively greater with time. At the end of ten and one half weeks, the first nine inches of soil contacting the hydrogen sulfide air mixture was sufficient to implement 100% removal.

An essential observation is that while bacterial population was declining, the efficiency of the soil for removing hydrogen sulfide was increasing.

These results suggest that at a concentration of 700 ppm hydrogen sulfide, a non-biological removal mechanism was operative. To help verify this hypothesis, further preliminary work was conducted using the same apparatus and an identical moist soil (4). Air flow was increased to six liters/minute and hydrogen sulfide flow to 200 milliliters/minute. The total flow of 6.2 liters/minute (1.12 cfm/ft^2) had a hydrogen sulfide concentration of 3.22 percent and introduced 282 ml. of hydrogen sulfide

per minute to the test column. Detention time was approximately 1.5 minutes. The following results were noted over a ten day period.

1. Temperature increases as high as 16°C were observed in the test column. No temperature increase occurred in the control column.
2. The zone of highest temperature moved up the column as time progressed, and the maximum temperature increase observed decreased as time progressed.
3. The soil layers first contacted by the gas mixture attained an air-dry moisture state, since no water was added. In this dry zone, the soil color changed from brown to black. In the upper soil region which remained moist, a yellowish color was observed, while the soil retained its brown color.
4. Reduction of hydrogen sulfide remained about 80% throughout the experiment.
5. In the test column, initial bacteria populations on heterotrophic specific and Thiobacillus specific medias dropped to essentially zero in the first 27 inches to be contacted by the hydrogen sulfide mixture, although this soil still removed hydrogen sulfide. Little change in bacteria population was noted in the control column.
6. Both elemental sulfur and sulfate ion increased in the test soil, but the former was approximately five times the latter.

Although Pomeroy (3) and Leiser (6, 7) concluded that microbiological growths were responsible for the oxidation of sewage odors and hydrogen sulfide, respectively, it is clear that other mechanisms are operating at high hydrogen sulfide concentrations. Perhaps more than one mechanism prevails at these high rates, as might be concluded from the two different colors observed in the soil under different moisture conditions.

III. THEORETICAL CONSIDERATIONS

As previously discussed, rapid biological removal of high concentrations of hydrogen sulfide was not observed. The chemical mechanistic alternatives are adsorption, water solution, ion exchange, and surface catalysis effects. The potential significance of each will be discussed separately in the following sections.

A. Adsorption

Before defining adsorption, let us look at what comprises a solid, and why its surface differs so markedly from the interior. The atoms or molecules which comprise the solid are held together by a combination of various forces: van der Waal's forces, homopolar valence forces, and electrostatic or Coulomb forces (8). While these forces are normally present in all solids, one usually predominates, such as Coulombic forces in ionic lattices, homopolar forces in atomic lattices, and van der Waal's forces in molecular lattices. Regardless of the nature of the forces involved, all atoms, ions, and molecules in the solid body are subjected to an equal force in all directions. But at the surface of a solid, atoms are subjected to unbalanced forces, the inward pull being greatest, thus creating a surface free energy. The surface free energy (a product of surface area and surface tension) is equal to the energy required to produce the surface. The tendency for spontaneous reduction of surface free energy may occur by reduction of surface area, surface tension, or both.

Adsorption of a liquid or gas upon a solid surface may be defined as a change in concentration at the interface from that in the bulk of the liquid or gas phase (9). When an atom or molecule is spontaneously adsorbed onto the solid surface, some of the unsaturated surface forces are balanced, thus decreasing the surface tension. Therefore spontaneous adsorption lowers the surface free energy (F). It should be noted that this decrease of surface

free energy may occur in both liquid-solid and gas-solid situations.

According to Brunauer (10), the entrophy (S) of the gas molecules decreases upon spontaneous adsorption, because the gas molecules are transformed from a three dimensional orientation to a two dimensional orientation, wherein they are either free to move upon the plane of the surface, or are rigidly locked in place. For isothermal changes, the following thermodynamic equation is true: $\Delta H = \Delta F + T\Delta S$, where

ΔH = Change in Enthalpy - Kcal/mole

ΔF = Change in Gibb's Free Energy - Kcal/mole

T = Temperature - °C

ΔS = Change in Entropy - Kcal/mole/°C

Hence, during a spontaneous isothermal adsorption in which ΔF and ΔS are negative, ΔH must also be negative, meaning that such spontaneous adsorptions are exothermic. This decrease in the system heat content is known as the heat of adsorption.

Most adsorptions may be conveniently classified into one of two categories, physical adsorption or chemical adsorption, the latter more widely known as chemisorption. The principal difference between the two classifications is determined by the interaction between the adsorbent, the solid material possessing the surface, and the adsorbate, the gas or vapor attached to this solid surface. Physical adsorption originates due to a weak interaction of the adsorbent and adsorbate caused by van der Waal's forces, the same forces active in condensation. Hence in a gas-solid situation physical adsorption is likened to condensation of a gas on a surface. The mechanism of chemisorption involves an interaction of electrons between the adsorbent and the adsorbate. The amount of this interaction varies,

the extremes being pictured as the adsorbate losing an electron to the adsorbent, the adsorbate becoming a positive ion, or the adsorbate gaining an electron from the adsorbent, and becoming a negative ion. In between these extremes lies the mechanism for the majority of chemisorption reactions. The principal characteristics of physical and chemical adsorption which allow them to be characterized as such (11) are shown in Table II.

The amount of adsorbate which will adsorb on a surface (X) is a function of pressure (or concentration), temperature, the nature of the gas, and the nature of the solid. Hence,

$$X = f\ (P, T, \text{gas}, \text{solid})$$

When the gas and solid to be studied are brought in contact under constant temperature conditions, the resultant relationship between the amount of gas adsorbed and the gas pressure may be presented graphically as an adsorption isotherm.

The Langmuir adsorption isotherm is a model derived on the basis of an equilibirum between the rate of adsorption and the rate of desorption. A Langmuir plot consists of plotting P/X/M versus P where:

P (or C) = pressure or concentration of the gas under study

X = weight of adsorbate

M = weight of adsorbent holding X weight units

Basic assumptions in the derivation of the model are (1) identical sites (as to energy of adsorption and any other property); (2) no interaction between adsorbed atoms; and (3) vibrational modes of the adsorbed atom parallel to the surface, rather than translation. Since monolayer formation is the maximum adsorption possible in the model, and chemical adsorption leads at

Table II: CHARACTERISTICS OF PHYSICAL ADSORPTION AND CHEMISORPTION (11)

Physical Adsorption	Chemisorption
Heat of adsorption less than about 10 kcal/mole	Heat of adsorption greater than about 20 kcal/mole
Adsorption is appreciably only at temperatures below the boiling point of the adsorbate	Adsorption can occur at high temperatures
The incremental increase in the amount adsorbed increases with each incremental increase in pressure of the adsorbate	The incremental increase in the amount adsorbed decreases with each incremental increase in the pressure of the adsorbate
The amount of adsorption on a surface is more a function of the adsorbate than the adsorbent	The amount of adsorption is characteristic of both adsorbate and adsorbent
No appreciable activation energy is involved in the adsorption process	An activation energy may be involved in the adsorption process
Multilayer adsorption occurs	Adsorption leads to, at most, a monolayer

most to a monolayer, Langmuirian plots of chemisorption data are usually linear. Success of fitting such a curve does not confirm the model or the assumptions used in its derivation, but merely indicates a first order reaction.

A purely empirical equation representing adsorption data was suggested by Freundlich, and is shown below:

$$X/M = K\, p^{n}$$

where X = weight of adsorbate

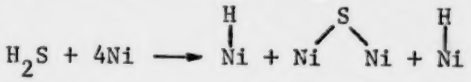
M = weight of adsorbent holding X weight units

P (or C) = pressure or concentration of the adsorbate

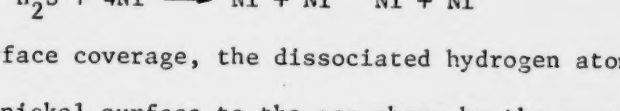
K and n = constants determined by the experiment

The equation represents an adsorption where successive incremental increases of pressure (or concentration) yield smaller amounts adsorbed, but in which there is no limit to the amount adsorbed. Whether or not the Freundlich isotherm is applicable may be tested by plotting log X/M versus log P. Such a plot should yeild a straight line with the slope equal to N and the intercept equal to K. Again, as with the Langmuir isotherm model, compliance with the model does not necessarily verify that the process occurring is one of adsorption.

One type of chemisorption deserving special attention is that of hydrogen sulfide gas upon artificially prepared heavy metal surfaces of the type that may be expected in soils. Den Besten and Selwood (12) explored the interaction between hydrogen sulfide gas and artificially prepared nickel surface. The mechanism of removal at low surface coverage was concluded to be attributable to the formation of four bonds per hydrogen sulfide molecule chemisorbed. The hypothesized reaction may be pictured as shown following:



At high surface coverage, the dissociated hydrogen atoms appeared to be forced from the nickel surface to the gas phase by the more strongly attracted sulfide atoms, as shown in the following reaction:



Approximately two thirds of the hydrogen atoms initially entering in the hydrogen sulfide molecule were eventually able to be removed as molecular hydrogen by degassing the nickel surface at high temperatures. The other one third was felt to be trapped between the nickel surface and the sulfide layer (12).

A similar dissociative chemisorption was also noted by Roberts and Ross (13) while investigating the interaction between hydrogen sulfide and artifically prepared iron surfaces. In this situation, no stoichiometric relationship between the hydrogen sulfide molecules and the iron atoms was mentioned by the authors. The suggested reaction appears below:

$$XFe(s) + H_2S(g) \longrightarrow Fe_XS(s) + H_2(g)$$

Thus, in the interaction of hydrogen sulfide with both nickel and iron surfaces, hydrogen gas is a product.

Siedlewski (14) has studied the adsorption interaction between activated carbon and hydrogen sulfide. The oxides of carbon were found to be the "active centers" responsible for the chemisorptive removal, but it was also found that these centers were not blocked by hydrogen sulfide adsorption. This appeared to be attributable to the ability of the activated carbon to act as a catalyst in the oxidation of hydrogen sulfide to sulfur, the sulfur then migrating away from these "active centers," therefore making the "active centers" available for further catalytic oxidation (14).

B. Water Solution

Solution of hydrogen sulfide gas in water present in the soil interstices and in the water film covering the soil surface may also be hypothesized as a potential removal mechanism. The minimum solubility of hydrogen sulfide in distilled water may be calculated using Henry's Law:

$$\bar{p} = Hx$$

Where: $\bar{p}$ = partial pressure of hydrogen sulfide in the gas phase--atmospheres

H = partial pressure of hydrogen sulfide in the gas phase in equilibrium with the solution--atmospheres/mole fraction

x = mole fraction of hydrogen sulfide soluble in the water under equilibrium conditions.

In order for Henry's Law to be valid, no ensuing chemical reaction with the solvent, other than ionization, should occur. Although calculations using Henry's Law do not produce exact results, they are normally correct to within a few percent, at partial pressures less than one atmosphere (9).

Using Henry's Law, the solubility of hydrogen sulfide in pH 7 distilled water was calculated at various water temperatures and hydrogen sulfide partial pressures, Table III. An example calculation used in constructing this table and the Henry's Law constants used in the calculations (15) may be found in the appendix.

C. Ion Exchange

Ion exchange differs from adsorption in that the former process releases from the soil an ion of like charge to that taken from solution. Soil fractions less than twenty microns in diameter (i.e. clay, silt and organic fractions) are generally felt to be the portions of the soil responsible for ion exchange reactions (16).

Three types of anion exchange mechanisms are possible in the soil. These mechanisms are:

1. The replacement of counter-ions which are held by the soil as the result of unequal force distribution within the crystal. Such sites for exchange may occur at broken surfaces, plane surfaces, and within the crystal structure itself. The unequal force distribution at these sites is attributed to the influence of low pH upon hydroxyl groups occurring in clays and hydrous oxides of iron and aluminum. For example, under acid conditions, a typical hydroxyl group from an inorganic crystal structure could behave as follows:

$$R\text{-}OH + H^+ + Cl^- \rightleftharpoons R\text{-}Cl + H_2O$$

with the chloride ion now acting as a counter-ion.

$$R\text{-}Cl + NO_3^- \rightleftharpoons R\text{-}NO_3 + Cl^-$$

TABLE III: CALCULATED MINIMUM SOLUBILITY OF HYDROGEN SULFIDE IN DISTILLED WATER

Milliliters of hydrogen sulfide which will dissolve in 100 grams of water at a gas pressure of 760 mm.

Temperature of H_2O - °C	Gas Phase Concentration of Hydrogen Sulfide - ppm						
	1	10	100	1000	10^4	10^5	Pure
0	4.65×10^{-4}	4.65×10^{-3}	4.65×10^{-2}	0.465	4.65	46.5	465
10	3.40×10^{-4}	3.40×10^{-3}	3.40×10^{-2}	0.340	3.40	34.0	340
20	2.58×10^{-4}	2.58×10^{-3}	2.58×10^{-2}	0.258	2.58	25.8	258
30	2.05×10^{-4}	2.05×10^{-3}	2.05×10^{-2}	0.205	2.05	20.5	205
40	1.67×10^{-4}	1.67×10^{-3}	1.67×10^{-2}	0.167	1.67	16.7	167
50	1.41×10^{-4}	1.41×10^{-3}	1.41×10^{-2}	0.141	1.41	14.1	141
60	1.21×10^{-4}	1.21×10^{-3}	1.21×10^{-2}	0 121	1.21	12.1	121
70	1.05×10^{-4}	1.05×10^{-3}	1.05×10^{-2}	0.105	1.05	10.5	105
80	9.22×10^{-5}	9.22×10^{-4}	9.22×10^{-3}	0.0922	0.922	9.22	92.2
90	8.65×10^{-5}	8.65×10^{-4}	8.65×10^{-3}	0.0865	0.865	8.65	86.5

The major factors determining the importance of this mechanism of anion exchange are the accessibility of hydroxyl groups, the geometry of the replacing anion, and the valence of the replacing anion (17).

2. Exchange of lattice ions is another prevalent mechanism. Such isomorphic replacement normally occurs at broken clay edges, but not on surfaces. A typical exchange of this occurs in the isomorphic displacement of hydroxyl ions from clays and hydrous oxides by fluorine ions. This may be pictured in the following way:

$$R\text{-}OH + F^- \rightleftharpoons R\text{-}F + OH^-$$

As in the previous mechanism, size and valence of the replacing anion are critical factors (18).

3. Although probably not of significance in this research, certain tetrahedral anions, such as phosphate, borate and arsenate, may extend the lattice by adsorption to the edges of silica tetrahedron. Note that these three anions are all of similar size to the silica tetrahedron. In terms of our definition of ion exchange, reactions of this type might be better classified as adsorptions.

Only in cases where a liquid film exists upon the soil particles could ion exchange be an anticipated hydrogen sulfide removal mechanism. Exchange mechanism two appears to be the only one of the three which could take place in this research. Mechanism one requires acidic conditions, such conditions favoring the hydrogen sulfide to remain primarily in the unionized aqueous form. Mechanism three requires a tetrahedral shape, which only sulfate possesses, and which H_2S, HS^-, and $S^=$ do not possess.

D. Contact Catalysis

Grant (19) has investigated the interaction between hydrogen sulfide and three types of activated carbon; 1) Pittsburgh Chemical Company type BPL, 2) type BPL impregnated with copper, and 3) type BPL impregnated with both copper and iron. Results indicate that both the copper and copper-iron impregnated carbons yield removal superior to the non-impregnated type BPL carbon, the copper-iron carbon being the more efficient of the two impregnated carbons studies. The principal purpose of the study was the determination of the hydrogen sulfide removal mechanism and the most efficient regeneration method for the spent carbon. Regeneration methods studied included steam purging, degassing, air purging, and various combinations of these three at varying temperatures and moisture conditions. The most effective regeneration technique was concluded by Grant (19) to be air purging at 100°C in the presence of a slight amount of water vapor; air purging at temperatures greater than 100°C yeilded no increase in regeneration efficiency, but regeneration at room temperature appeared to be only partially effective.

During passage of hydrogen sulfide over the copper impregnated carbon, the carbon changed color from black to blue; while the iron-copper impregnated carbon changed from red to black upon contact with hydrogen sulfide. These color changes were felt by Grant (19) to indicate the formation of blue cupric sulfide from black cupric oxide, and of black iron sulfide from red ferric oxide. Upon regeneration with room temperature air, the original color of the carbon returned, except that yellow deposits were noted on the carbon surface. These deposits were identified as amorphous sulfur.

Several removal mechanisms were postulated to account for the increased removal capacity of the impregnated carbons over the unimpregnated type BPL

carbon, which removed the hydrogen sulfide by physical adsorption. Grant (19) suggested that the equations defining the removal process were:

$$CuO + H_2S \longrightarrow CuS + H_2O$$

$$Fe_2O_3 + 3H_2S \longrightarrow 2FeS + S + 3H_2O$$

$$Fe_2O_3 + 3H_2S \longrightarrow Fe_2S_3 + 3H_2O$$

In addition, Grant (19) hypothesized the following equations defining the regeneration by air oxidation:

$$CuS + 1/2O_2 \longrightarrow CuO + S$$

$$2FeS + 3/2O_2 \longrightarrow Fe_2O_3 + 2S$$

$$Fe_2S_3 + 3/2O_2 \longrightarrow Fe_2O_3 + 3S$$

One specific problem of hydrogen sulfide removal pertains to the removal of hydrogen sulfide from natural gas, prior to its delivery to the customer. Although the hydrogen sulfide may be removed by "wet" chemical processes, the most common method used is the passage of the gas over a solid adsorbent, usually iron oxide or zinc oxide (20).

Griffith and Morcom (21) studied the interaction between hydrogen sulfide mixed with natural gas and seven forms of ferric oxide, αFe_2O_3, $\alpha Fe_2O_3 \cdot H_2O$, $\beta Fe_2O_3 \cdot H_2O$, ∂Fe_2O_3, $\partial Fe_2O_3 \cdot H_2O$, $\delta Fe_2O_3 \cdot H_2O$ and amorphous Fe_2O_3. Identification of the various ferric oxide forms was determined by the rate of change of their magnetic properties on heating and their rate of solution in a standard acid solution. Griffith and Morcom (21) indicate that all forms, except the β form react with hydrogen sulfide to yield a hydrated ferric sulfide, as shown below:

$$2Fe_2O_3 \cdot H_2O + 6H_2S \longrightarrow 2Fe_2S_3 \cdot H_2O + 6H_2O$$

$$2Fe_2O_3 + 6H_2S \longrightarrow 2Fe_2S_3 \cdot H_2O + 6H_2O$$

Their results also indicated that the hydrated ferric sulfide may be readily oxidized back to ferric oxide when the temperature is less than 50°C and the pH greater than seven. Under dry conditions, the authors

found that the $Fe_2S_3 \cdot H_2O$ is oxidized to $\alpha Fe_2O_3 \cdot H_2O$, but under moist conditions, the oxidation product is $\partial Fe_2O_3 \cdot H_2O$. At temperatures greater than 50°C, dehydration of the $Fe_2S_3 \cdot H_2O$ occurred, and the resulting anhydrous sulfide oxidized very slowly. In addition, the Fe_2S_3 produced by dehydration was found to decompose, yielding FeS_2 and Fe_8S_9. When these latter two forms were oxidized, they yielded respectively, ferric sulfate and a completely inactive ferric oxide.

Not all of the oxide forms studied by Griffith and Morcom (19) showed identical removal capabilities. The $\alpha Fe_2O_3 \cdot H_2O$ and $\partial Fe_2O_3 \cdot H_2O$ gave the best removals, the $\alpha Fe_2O_3 \cdot H_2O$ being slightly superior. An interesting situation occurred when some of the less active oxides were reduced to the sulfide form, and then oxidized in a dry environment, thus being converted to the very active $\alpha Fe_2O_3 \cdot H_2O$ form. Because $\alpha Fe_2O_3 \cdot H_2O$ possessed the best removal capability, a relatively inactive form was converted to the most active form observed by a sulfiding-oxidation cycle.

E. Summary

For the removal of H_2S by dry, sterile soil, adsorption and surface catalysis appear to be the mechanisms which could be operative. Due to the relatively large surface areas presented by soil, adsorption appears to be a likely prospect. However, the large percentage of metals in soil suggests that surface catalysis reactions may also be prevelant.

Naturally, it is logical to expect some hydrogen sulfide removal by water solution in wet soils. No information is available to determine the rate of solution. Once solution of hydrogen sulfide takes place, the exchange of one of its ionized forms with lattice ions in the soil appears to be possible. Therefore, removal by moist soils depends upon the rate of hydrogen sulfide solution in water.

IV. EXPERIMENTAL METHODS

A. Apparatus Used

Gas-Soil Uptake of Hydrogen Sulfide

Five-hundred milliliter Erlenmeyer flasks stoppered with black rubber stoppers were utilized for gas-soil uptake tests. Each stopper had a one and one-half inch piece of glass tubing through it. Serum caps were used to cover the glass tubing.

Liquid-Soil Uptake of Hydrogen Sulfide

Standard three-hundred milliliter BOD incubation bottles with glass stoppered tops were utilized for liquid-soil uptake tests. A magnetic stirrer was used to keep the soil in continual motion during the uptake period.

Vacuum Pump

A Precision Model 75 Vacuum Pump capable of delivering a vacuum of 0.1 micron or better was utilized for evacuation of dessicators used in surface area determinations.

Centrifuge

An International centrifuge, size 1, Type B, was used to separate the soil from the liquid phase cation solution during the cation saturation treatment of the soil.

Dynamic Uptake Test Columns

Columns to contain the soil were constructed from clear plastic tubing, two and one-quarter inches inside diameter and eight and one-half inches tall. Gas movement was from bottom to top. The lower two inches were filled with Raschig rings to facilitate gas distribution across the entire column cross section. A thin layer of glass wool was placed between the

rings and the soil to prevent settlement of the soil into the lower ring packed portion of the column. Rubber stopers fitted with a glass "tee" were used to cover each end of the column, influent and effluent samples were taken from the base of the "tee."

B. Experimental Techniques

Gas-Solid Uptake Tests

A modification of the methylene blue method suggested by Jacobs (22, 23) was adapted for the testing of gaseous hydrogen sulfide samples. This modification was necessary due to the high concentration of the samples tested. The modification entailed an increase of the color developing reagents, the ferric chloride solution and the N,N-dimethyl-p-phenylenediamine-sulfuric acid solution, to the concentration where they were slightly in excess of the amount required for maximum color development. Extreme care had to be exercised to maintain the sulfuric acid solution only slightly in excess, or results tended to be erratic.

To determine the equilibrium concentration in the Erlenmeyer flasks, a three milliliter gas sample was withdrawn from the flasks and injected into a stoppered twenty milliliter test tube, containing ten milliliters of cadmium hydroxide adsorption solution. Precipitation of the hydrogen sulfide in this sample was achieved by several seconds of rapid hand shaking of the test tube. Color developing reagents were then added to the absorption solution container, followed by dilution to 25 milliliters. This diluted sample was analyzed at a wavelength of 760 mμ using a Beckman model DU spectrophotometer. A standard curve was used to convert the absorbance reading obtained spectrophotometrically to concentration of hydrogen sulfide.

Liquid-Solid Uptake Tests

In running the liquid-solid uptake tests, one gram of soil and a varying amount of sodium sulfide solution were mixed with the exact amount of a de-oxygenated buffer mixture to completely fill the glass stoppered bottle. By this method, no gas phase was allowed to be present during the test. The bottles were placed upon magnetic mixers in constant temperature rooms, and stirred until attainment of equilibrium. Composition of the buffer mixtures used may be found in Appendix C.

The concentration of total sulfide remaining at equilibrium was determined by a modified titrimetric method (24). Twenty-five milliliter samples were withdrawn from the stoppered bottles and added to a mixture of five milliliters of concentrated hydrochloric acid and five milliliters of 0.025 N iodine solution. The iodine remaining after oxidation of the added hydrogen sulfide was back titrated with 0.025 N sodium thiosulfate solution, using starch indicator. The calculations for concentration were preformed as suggested by Standard Methods (24).

The apparatus and technique for uptake studies on the disodium salt of Ethylenediaminetetraacetic acid (abbreviated EDTA) were identical to that for sulfide uptake, with the exception that EDTA was substituted for sodium sulfide. A modification of the normal EDTA titration method (24) for water hardness was used for EDTA determination at equilibrium. In this modified method, the titrant used was the equilibrium EDTA-buffer mixture taken from the glass stoppered bottle, while the sample being titrated was prepared from a standard sodium solution and an ammonium buffer solution. Calculations were performed as follows:

$$\frac{\text{mg. EDTA Uptake}}{\text{wt. of soil used}} = \frac{(\text{ml Ca std. used})}{\text{ml titrated from bottle containing soil}} - \frac{\frac{\text{mg equivalent of EDTA}}{\text{ml std. Ca solution}}}{\text{ml titrated from blank}} \times 300 \text{ ml.}$$

where three-hundred was the volume of the glass stoppered bottles in milliliters, and the blank was prepared in identical fashion to the other bottles, with the exception that it contained no soil.

Surface Area Determination

A modification of the ethylene glycol monoethyl ether (EGME) method (25) was used to determine soil surface area. The recommended procedure called for replacement of all "fixed" cations in the soil with calcium, because it was felt that such fixation with calcium would create more uniform and reproducible results. However, others have found that when determining soil surface area using ethylene glycol, the saturating cation used determined to a great extent the amount of ethylene glycol retained (26). In this research, it was felt that altering the cation status in any way was likely to give surface area measurements different from the surface area actually contacted by the hydrogen sulfide. Therefore, no calcium washing was used when determining soil surface areas. Phosphorous pentoxide was used as the dessicant at all times, except for the first evacuation after the addition of EGME, at which time calcium chloride was used.

Soil Sulfur and Sulfate Testing

In the determination of elemental sulfur, the acetone extraction method recommended by Simon and Schollenberger was used (27). A turbidimetric determination was selected for the measurement of sulfate (28).

Soil Preparation

Sterilized soils were obtained by placing the soil in a 103°C oven for four days. After this time, no viable organisms could be isolated from the soil on nutrient agar or medias specific for heterotrophic or Thiobacillus bacteria.

Cation saturation was achieved by washing the soil twice with a 10% solution of the chloride salt of the cation desired to saturate the soil exchange sites. Next, quadruple washings with distilled water removed all "free" cations remaining in the saturated soil. All washings took place in plastic centrifuge tubes to alleviate any error due to transferes between the centrifuge tubes and other equipment.

Physical characteristics of Lynden loam, Appendix I, were obtained using ASTM recommended testing procedures (29).

Dynamic Soil Testing

Both wet and dry sterile soils were used in the dynamic uptake testing. Wet soils were prepared from the dry state by spraying water from an atomizer onto a soil sample which was continually mixed. No attempts were made to introduce additional water to the soil once testing began, due to the short term nature of the tests. Although it was realized that more accurate results would have been attained by keeping the soil at a constant equilibrium moisture content through continual water addition, the results attained appear to sufficiently demonstrate the influence of moisture upon hydrogen sulfide removal in a dynamic system.

In the tests requiring soil rejuvenation, the soil was removed from the column and spread out overnight on a newspaper at room temperature to allow contact with air. In all dynamic testing, influent and effluent samples were

taken immediately as the gas stream entered and emerged from the soil column. Breakthrough time was selected as the time when the effluent concentration reached 5% of the influent concentration.

V. RESULTS

A. Liquid-Soil Batch Uptake Tests

Using the apparatus and technique described, the ability of unaltered sterile soils and prepared cation saturated sterile soils to remove sulfide from solution was investigated. The majority of this testing was conducted at pH 5.8, since this was the natural pH of Lynden loam. Although the addition of sodium sulfide tended to slightly increase the pH of the buffered solution, the buffer possessed sufficient strength to maintain the solution pH to within 0.2 pH units of that desired at all times. In spot checks using a much more concentrated buffer solution, no pH change was observed, but identical removals were obtained.

The passing two-hundred sieve fraction of sterile Lynden loam was used to determine the influence of solution pH upon soil removal ability. As shown by Figure 2, the best removal occurred at pH 8.0, lesser removal occurring at lower pH values. The strong dependence of removal upon temperature at pH values of 5.8 and 8.0 may be seen in Figure 3. Note that Figure 3 illustrates the equilibrium position, and in no way is intended to illustrate a rate effect.

Using sterile Lynden loam soil, the influence of sieve size upon removal at equilibrium is illustrated in Figure 4. In this figure, it can be seen that the best removal per gram of soil was produce by the smallest grain size fraction (largest sieve number), indicating that possibly soil surface area influences removal ability, assuming constant soil composition.

The influence of equilibrium removal ability of the passing two-hundred fraction of sterile Lynden loam when saturated with various common cations appears in Figures 5 and 6. The "washed" soil underwent four washings with distilled water, but otherwise no changes were made in the cation status.

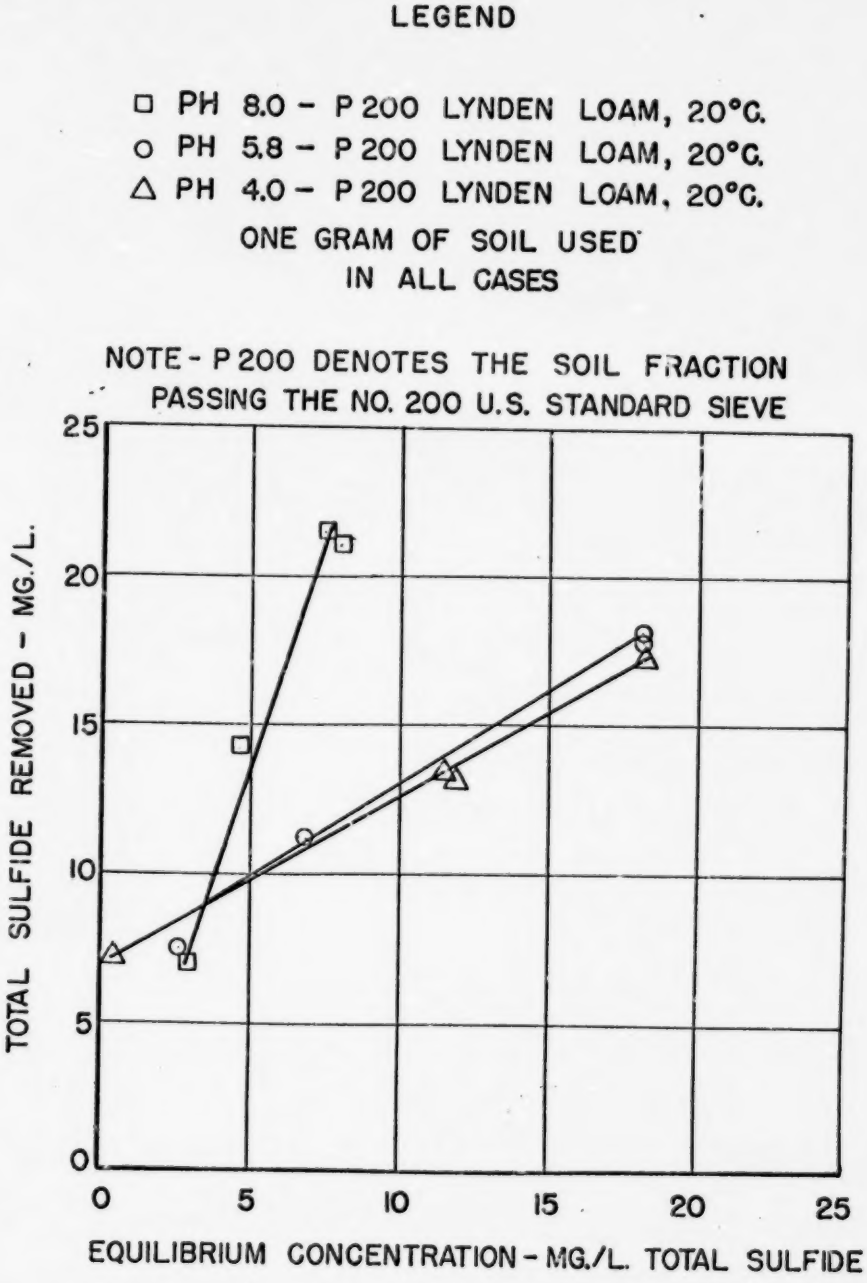

LEGEND
□ PH 8.0 – P 200 LYNDEN LOAM, 20°C.
○ PH 5.8 – P 200 LYNDEN LOAM, 20°C.
△ PH 4.0 – P 200 LYNDEN LOAM, 20°C.
ONE GRAM OF SOIL USED IN ALL CASES
NOTE - P 200 DENOTES THE SOIL FRACTION PASSING THE NO. 200 U.S. STANDARD SIEVE
TOTAL SULFIDE REMOVED - MG./L.
0
5
10
15
20
25
EQUILIBRIUM CONCENTRATION - MG./L. TOTAL SULFIDE

FIGURE 2 - PH INFLUENCE ON SULFIDE UPTAKE IN LIQUID-SOIL SYSTEMS

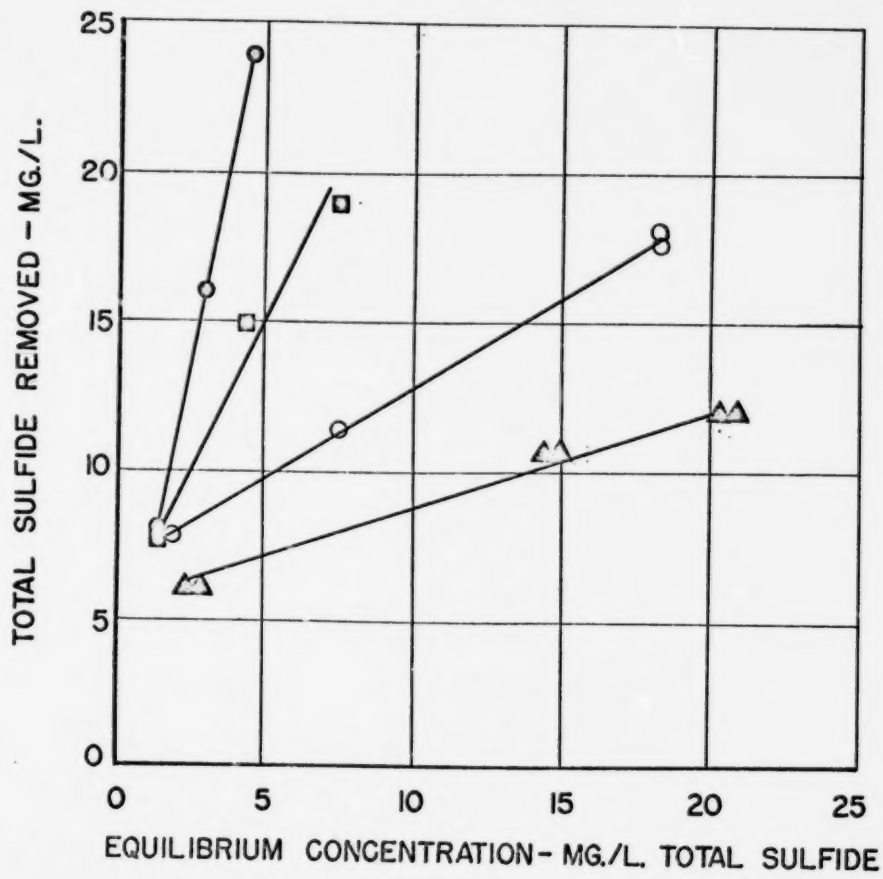

LEGEND
45°C. – P 200 LYNDEN LOAM, PH 8.0
45°C. – P 200 LYNDEN LOAM, PH 5.8
20°C. – P 200 LYNDEN LOAM, PH 5.8
5°C. – P 200 LYNDEN LOAM, PH 5.8
ONE GRAM OF SOIL USED IN ALL CASES
TOTAL SULFIDE REMOVED – MG./L.
0
5
10
15
20
25
EQUILIBRIUM CONCENTRATION – MG./L. TOTAL SULFIDE

FIGURE 3 – TEMPERATURE INFLUENCE ON SULFIDE UPTAKE IN LIQUID – SOIL SYSTEMS

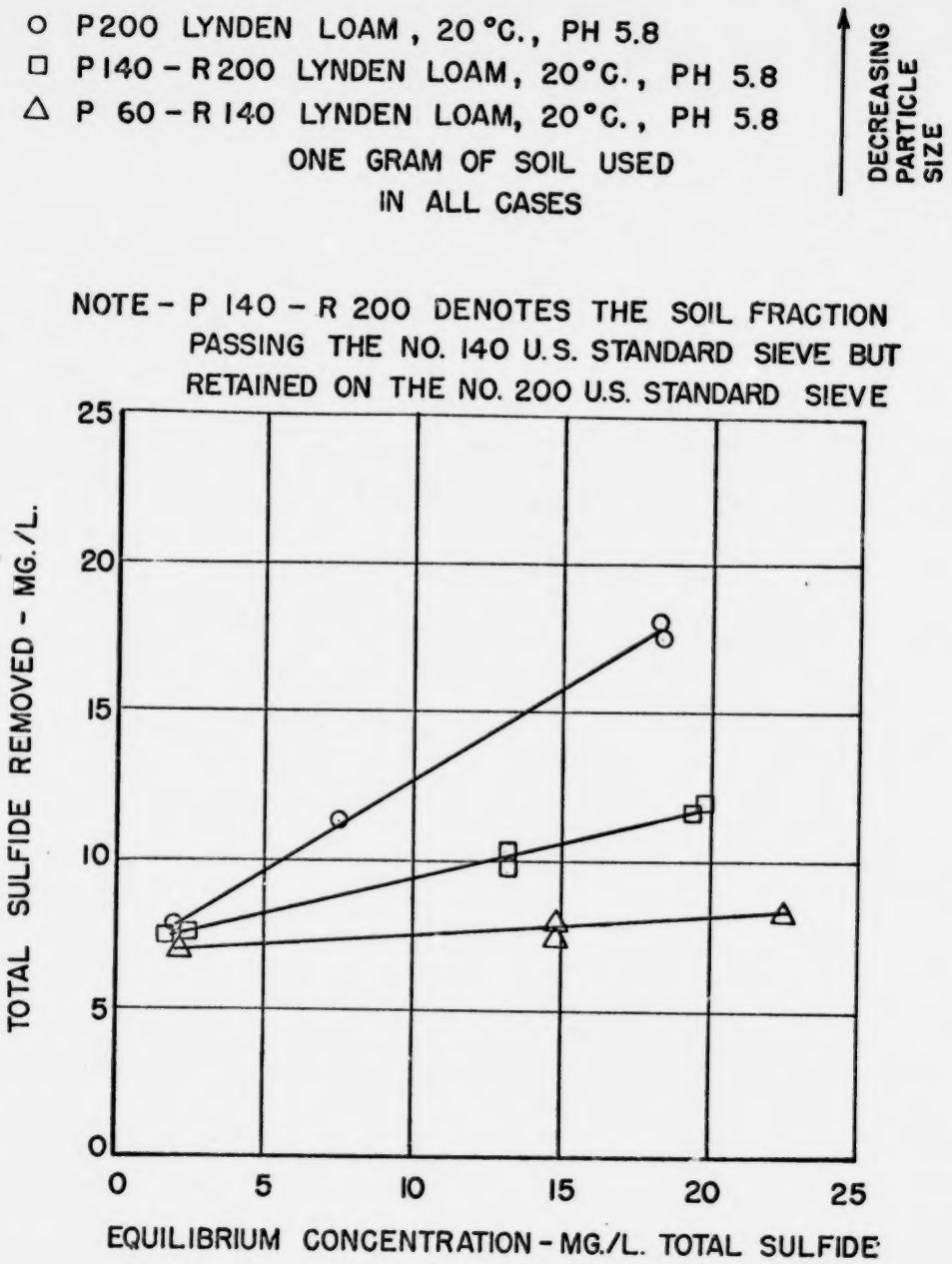

LEGEND
○ P200 LYNDEN LOAM, 20°C., PH 5.8
□ P140 - R200 LYNDEN LOAM, 20°C., PH 5.8
△ P 60 - R140 LYNDEN LOAM, 20°C., PH 5.8
ONE GRAM OF SOIL USED IN ALL CASES
DECREASING PARTICLE SIZE
NOTE - P 140 - R 200 DENOTES THE SOIL FRACTION PASSING THE NO. 140 U.S. STANDARD SIEVE BUT RETAINED ON THE NO. 200 U.S. STANDARD SIEVE
TOTAL SULFIDE REMOVED - MG./L.
0
5
10
15
20
25
EQUILIBRIUM CONCENTRATION - MG./L. TOTAL SULFIDE

FIGURE 4 - SIEVE SIZE INFLUENCE ON SULFIDE UPTAKE IN LIQUID - SOIL SYSTEMS

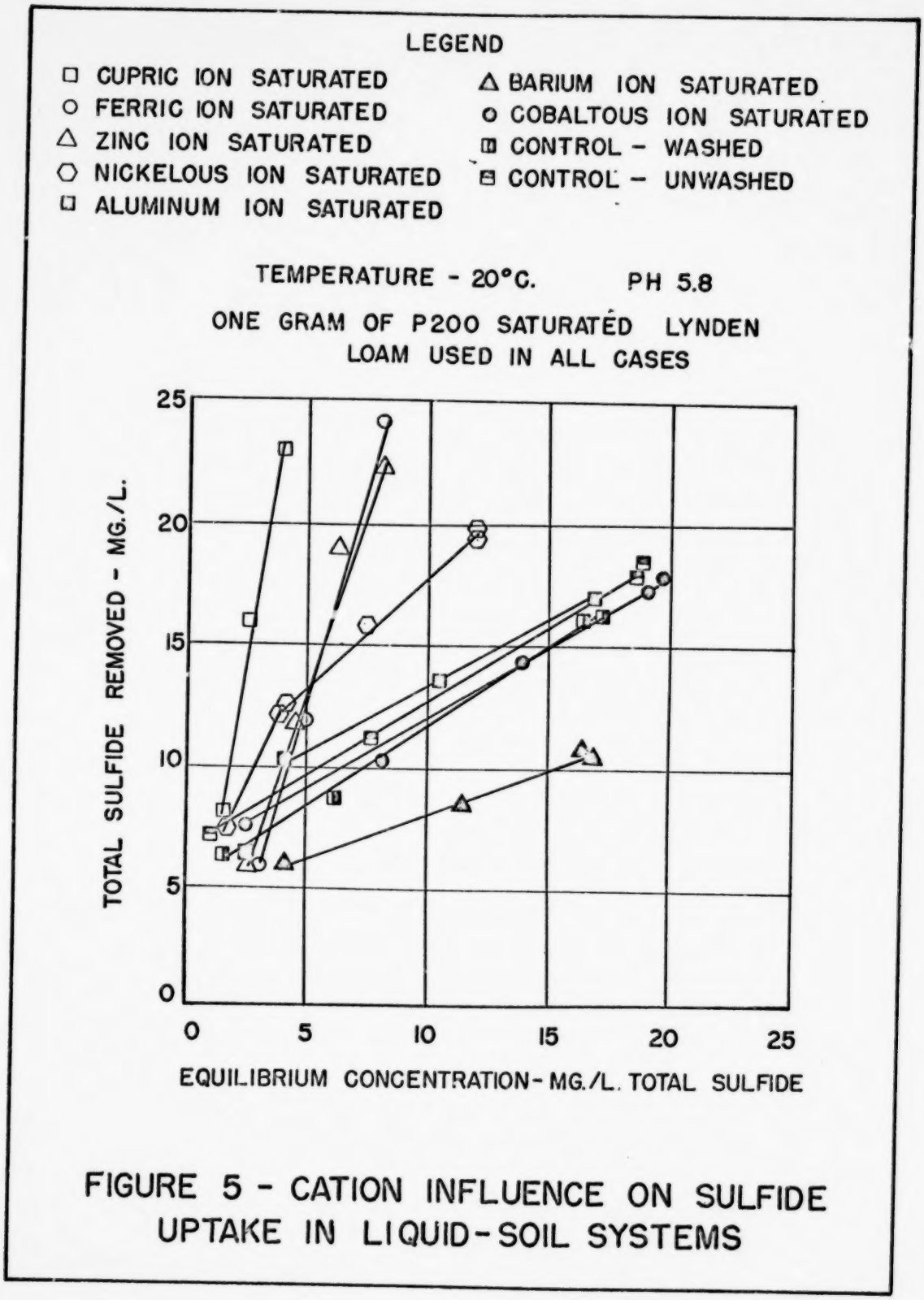


FIGURE 5 - CATION INFLUENCE ON SULFIDE UPTAKE IN LIQUID-SOIL SYSTEMS

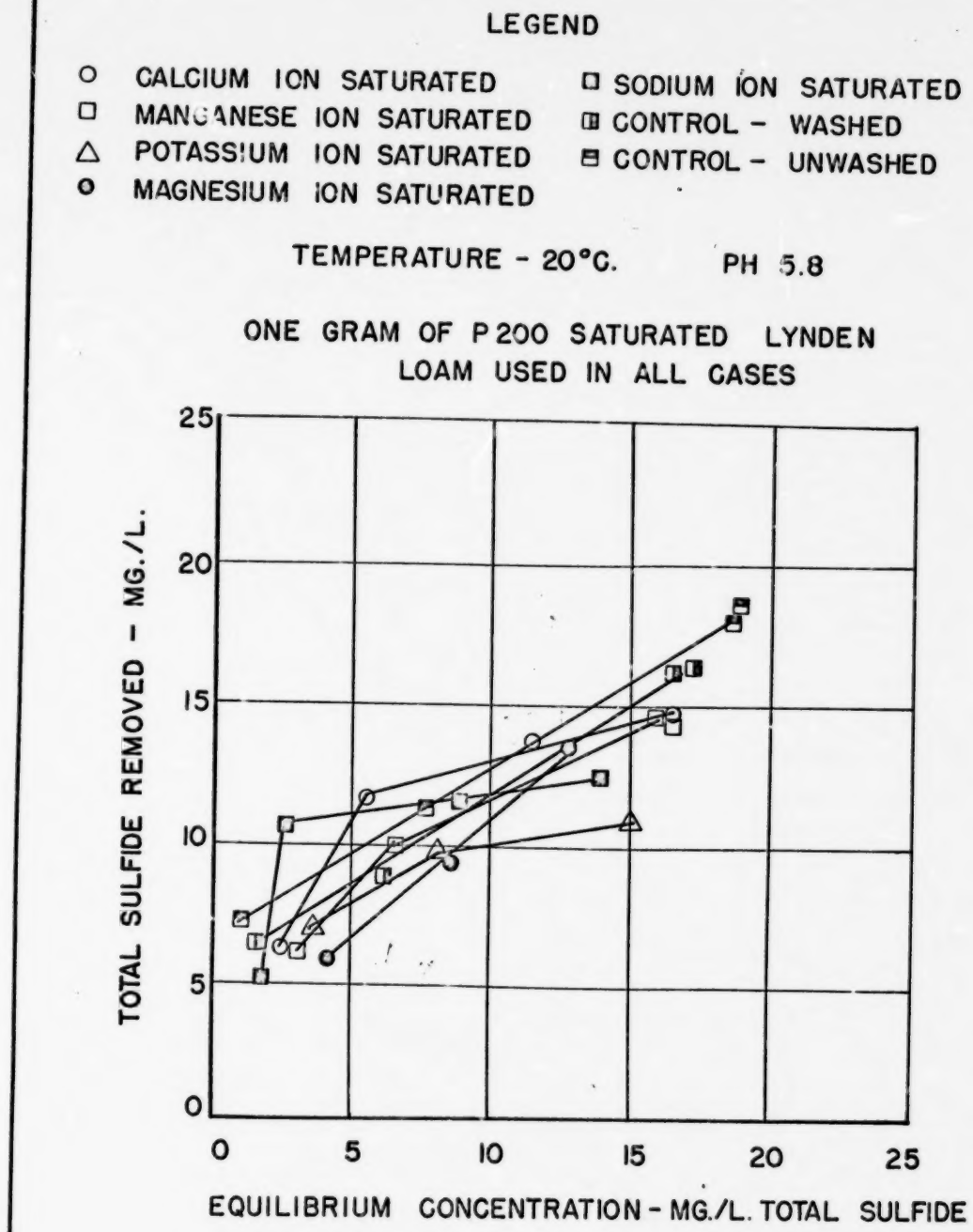


FIGURE 6 - CATION INFLUENCE ON SULFIDE UPTAKE IN LIQUID-SOIL SYSTEMS

The relationship between equilibrium removal capacity of the passing two-hundred fraction of sterile Lynden loam and a typical clay, sand, and humic soil (all sterile) may be observed in Figure 7. Elemental chemical analyses of the soils studied may be found in Tables VII and VIII.

Isotherms for data collected for sterile Lynden loam are presented according to the Freundlich and Langmuir isotherm models in Figures 8 and 9 respectively.

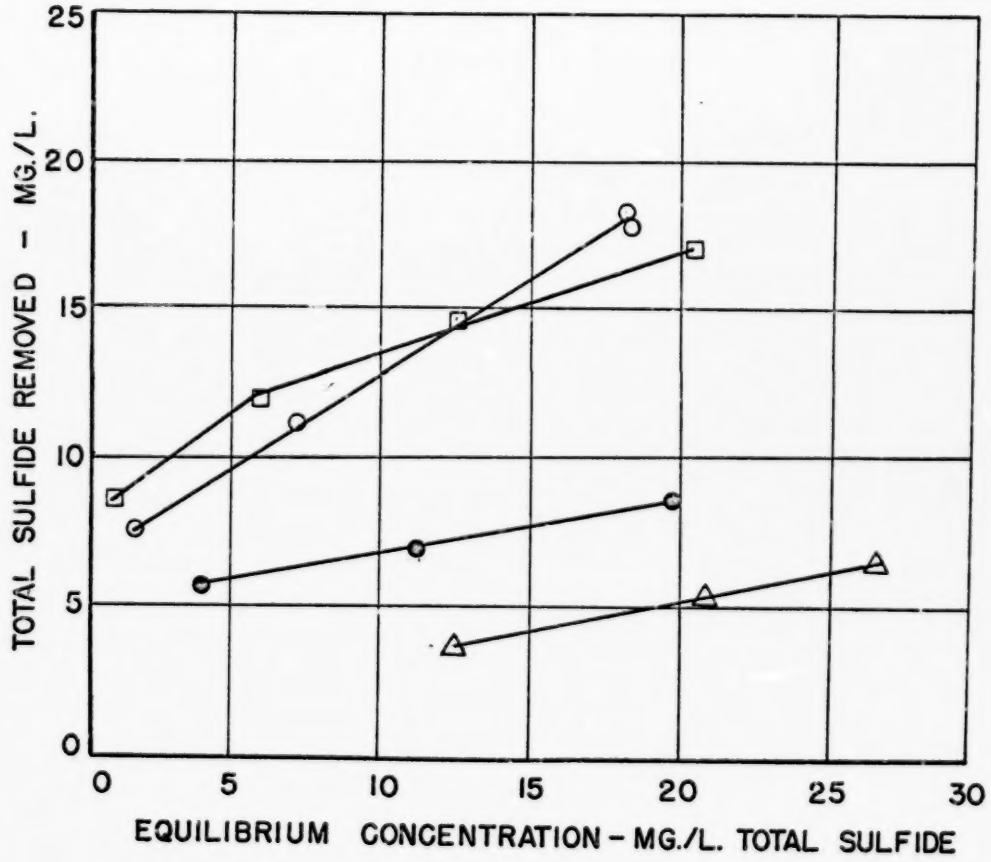


FIGURE 7 - SULFIDE UPTAKE BY SEVERAL SOILS IN LIQUID-SOIL SYSTEMS

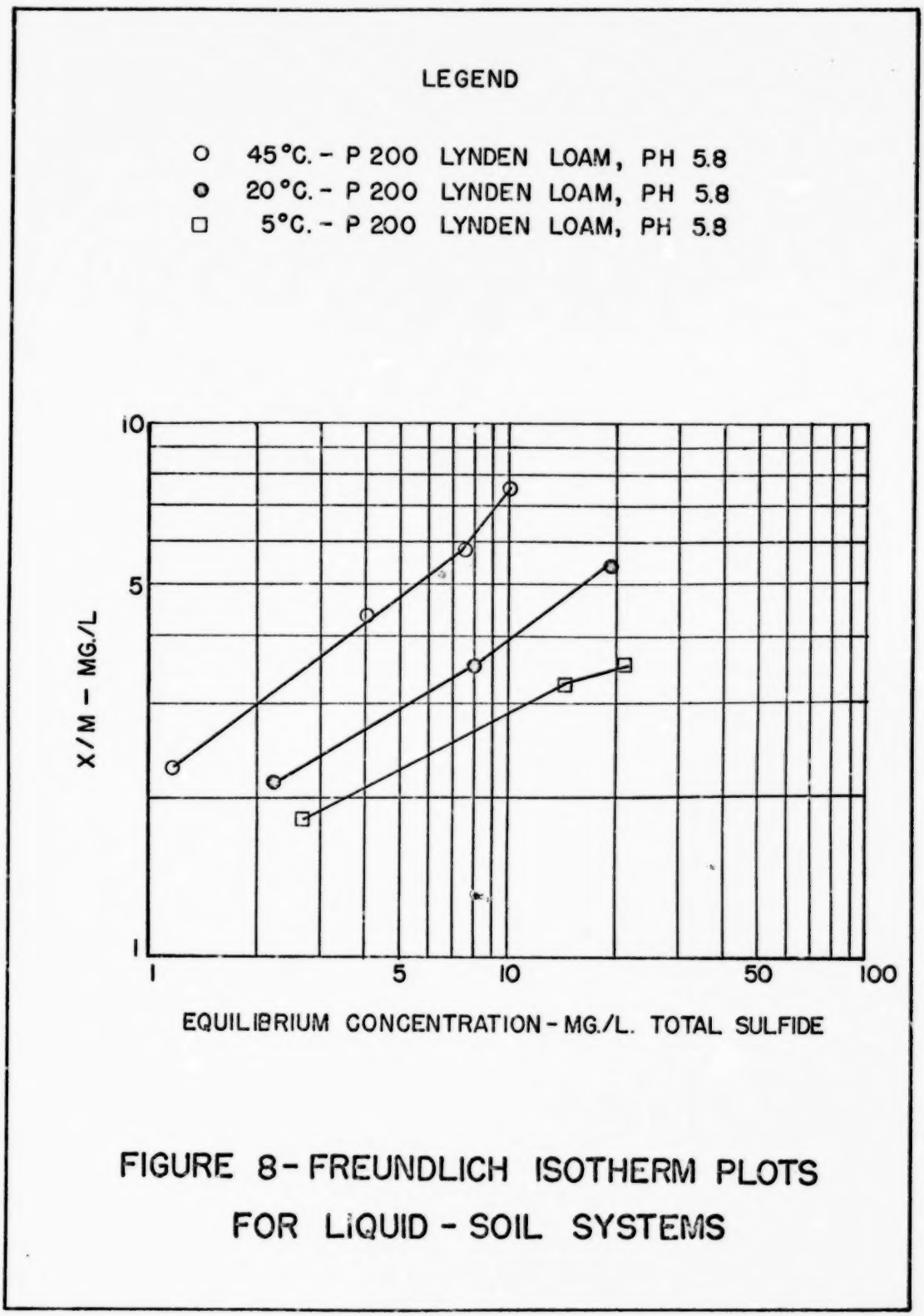


FIGURE 8 - FREUNDLICH ISOTHERM PLOTS FOR LIQUID - SOIL SYSTEMS

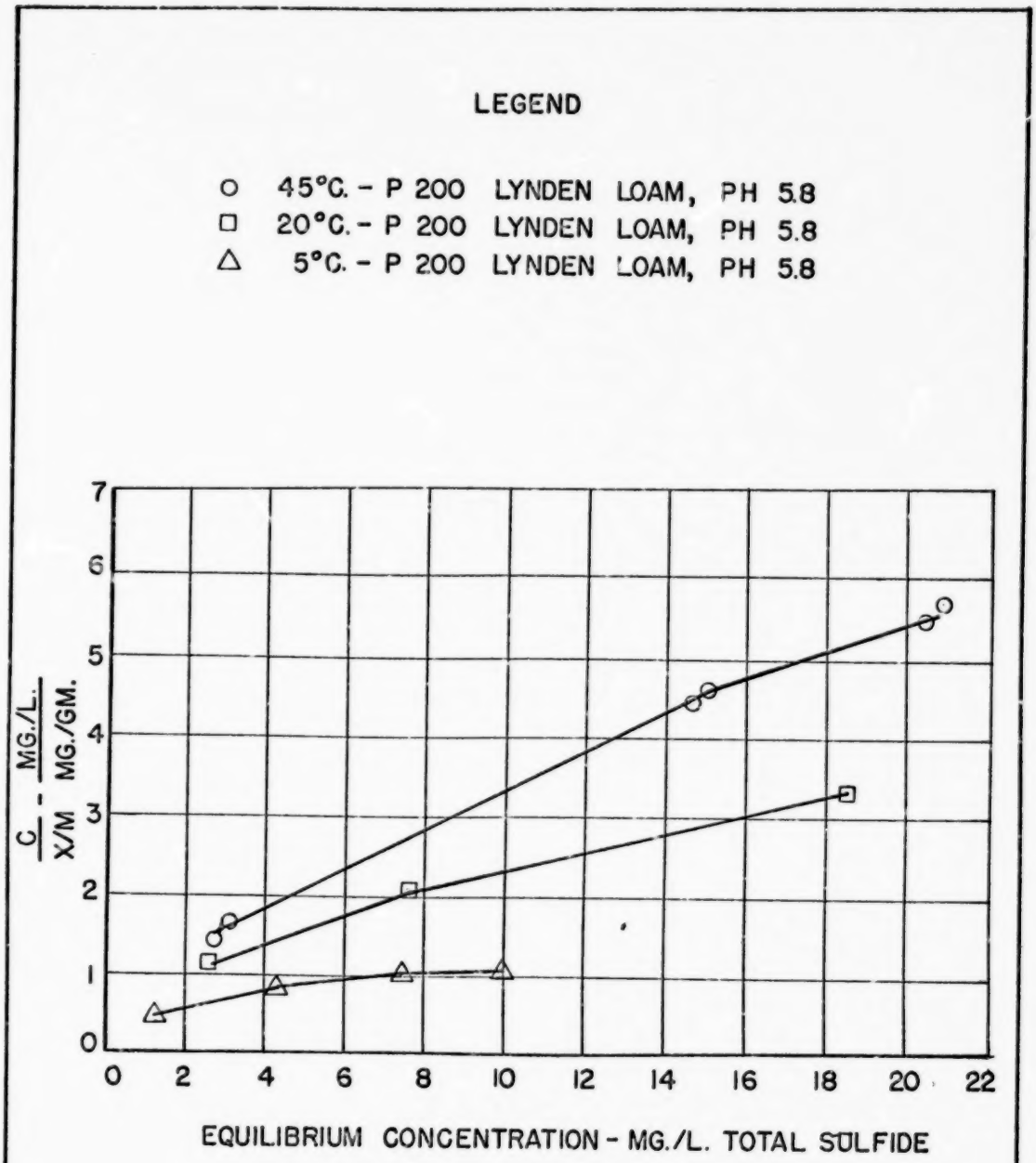


FIGURE 9 - LANGMUIR ISOTHERM PLOTS FOR LIQUID - SOIL SYSTEMS

B. Gas-Soil Batch Uptake Tests

The capacity of dry soils to remove hydrogen sulfide from the gas phase was investigated using the previously described equipment. The temperature influence upon removal by the passing number 200 sieve fraction of sterile Lynden loam appears in Figure 10. Figures 12 and 13 show respectively Freundlich and Langmuir isotherm plots for various sieve fractions of sterile Lynden loam. Two larger size fractions of Lynden loam were also studied, the comparison between the uptake isotherms of these sterile fractions and the passing no. 200 sieve fraction may be seen in Figure 11. The influence of cation saturation upon the uptake isotherm of the passing no. 200 sieve fraction of sterile Lynden loam was also investigated. Results from these tests are shown in Figures 14 and 15. In these tests, the "washed" sample underwent four successive washings with distilled water, but the cation balance was unaltered in any other way. The uptake curve for unwashed p200 Lynden loam is also shown in Figures 14 and 15.

In addition to Lynden loam, a humic, a clay, and a sand soil (all sterile) were also studied to determine their ability to remove hydrogen sulfide from the gas phase. An uptake isotherm of the passing no. 200 sieve fraction for each of these sterile soils and also for Lynden loam appears in Figure 16.

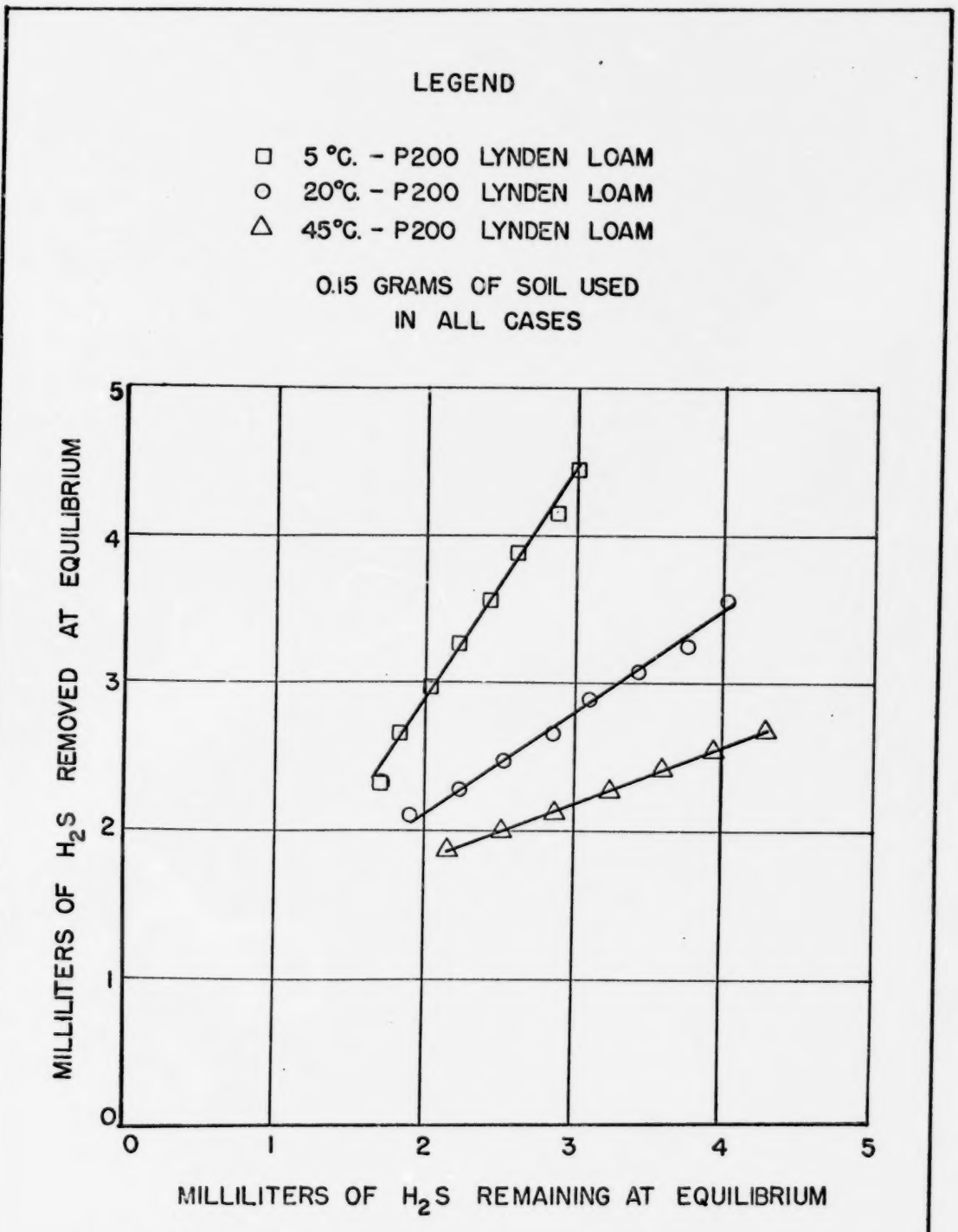


FIGURE 10 - TEMPERATURE INFLUENCE ON HYDROGEN SULFIDE REMOVAL IN GAS - SOIL SYSTEMS

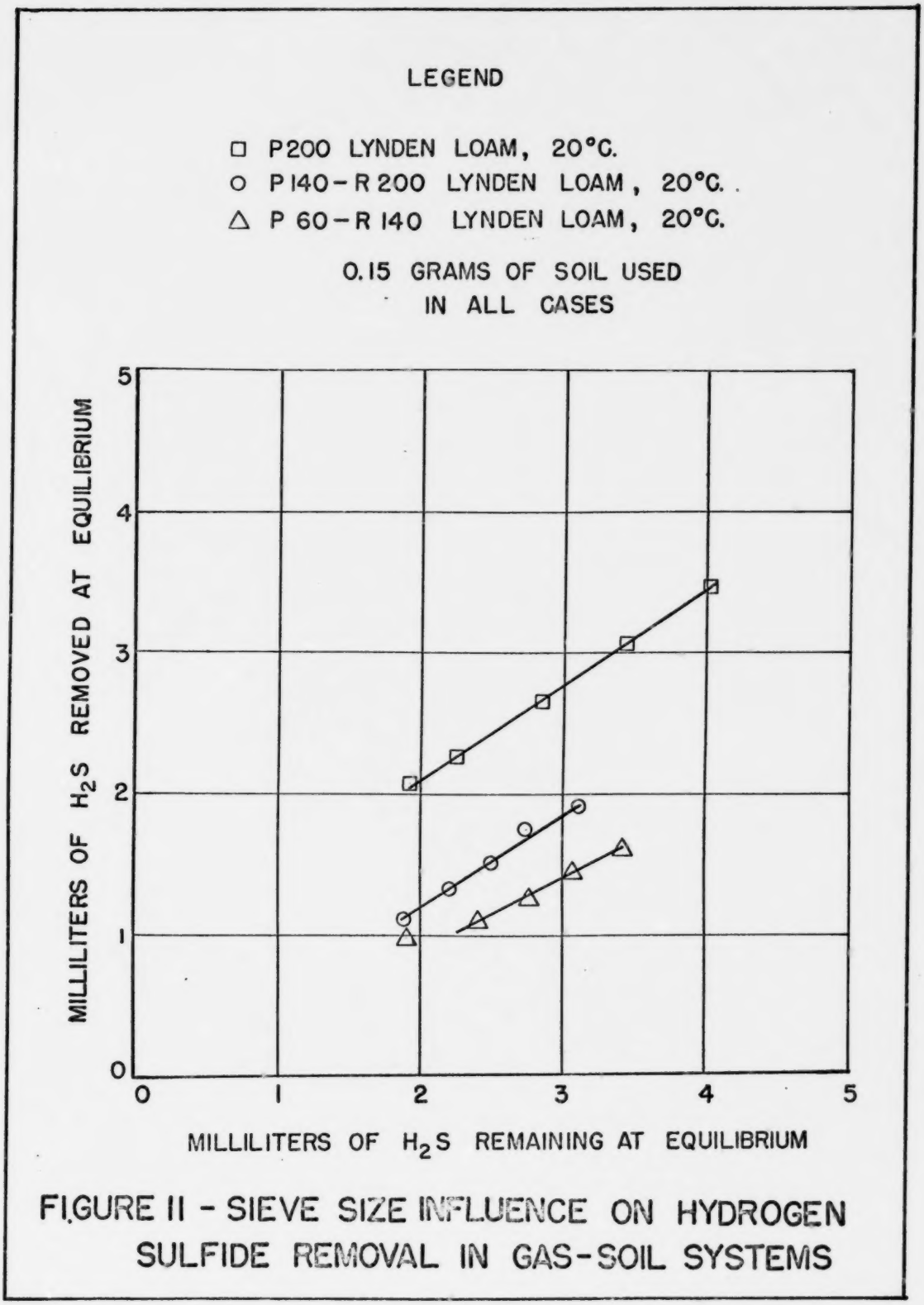


FIGURE II - SIEVE SIZE INFLUENCE ON HYDROGEN SULFIDE REMOVAL IN GAS-SOIL SYSTEMS

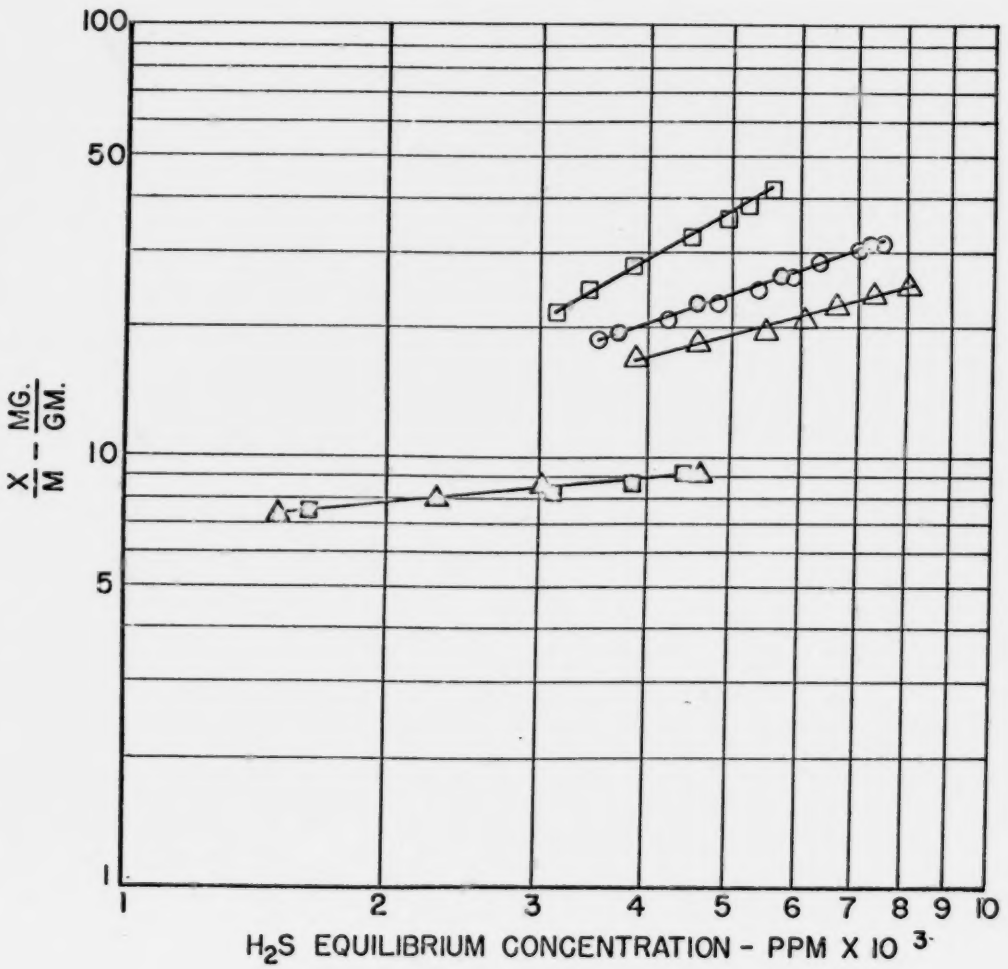


FIGURE 12 - FREUNDLICH ISOTHERM PLOTS OF GAS - SOIL SYSTEMS

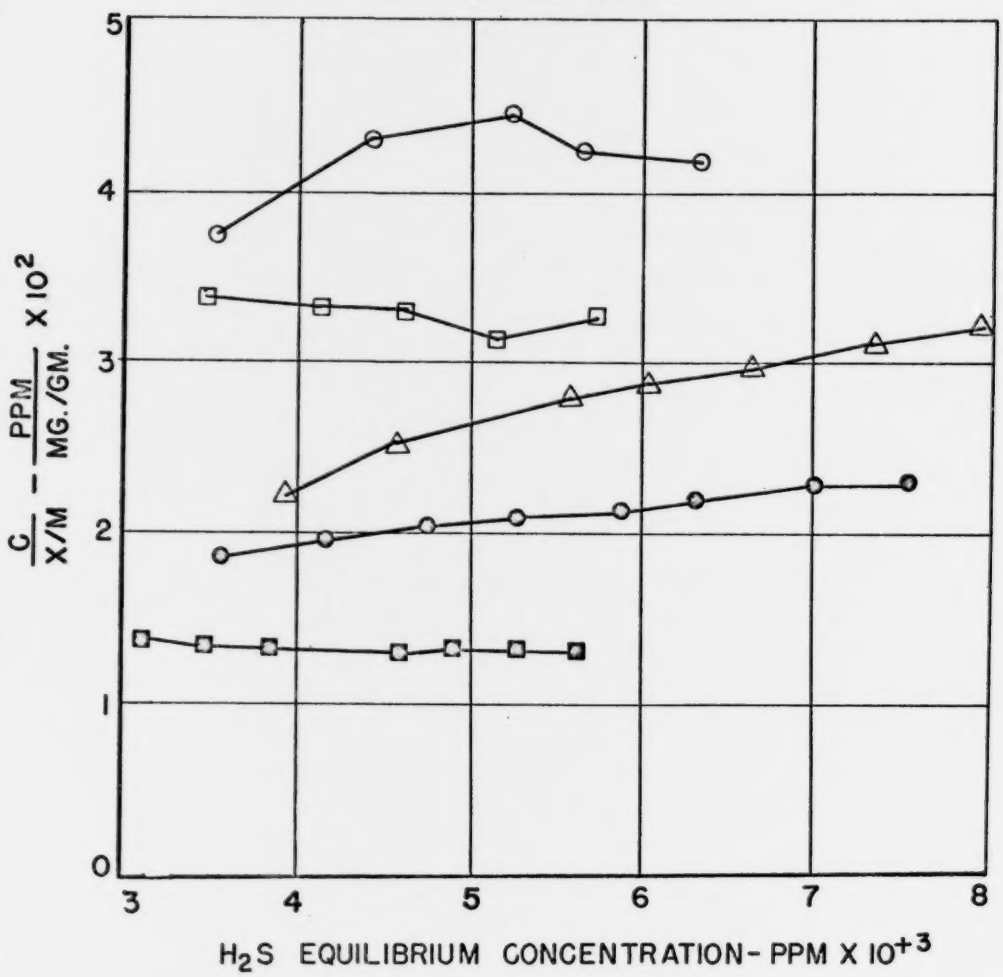


FIGURE 13 - LANGMUIR ISOTHERM PLOTS FOR GAS - SOIL SYSTEMS

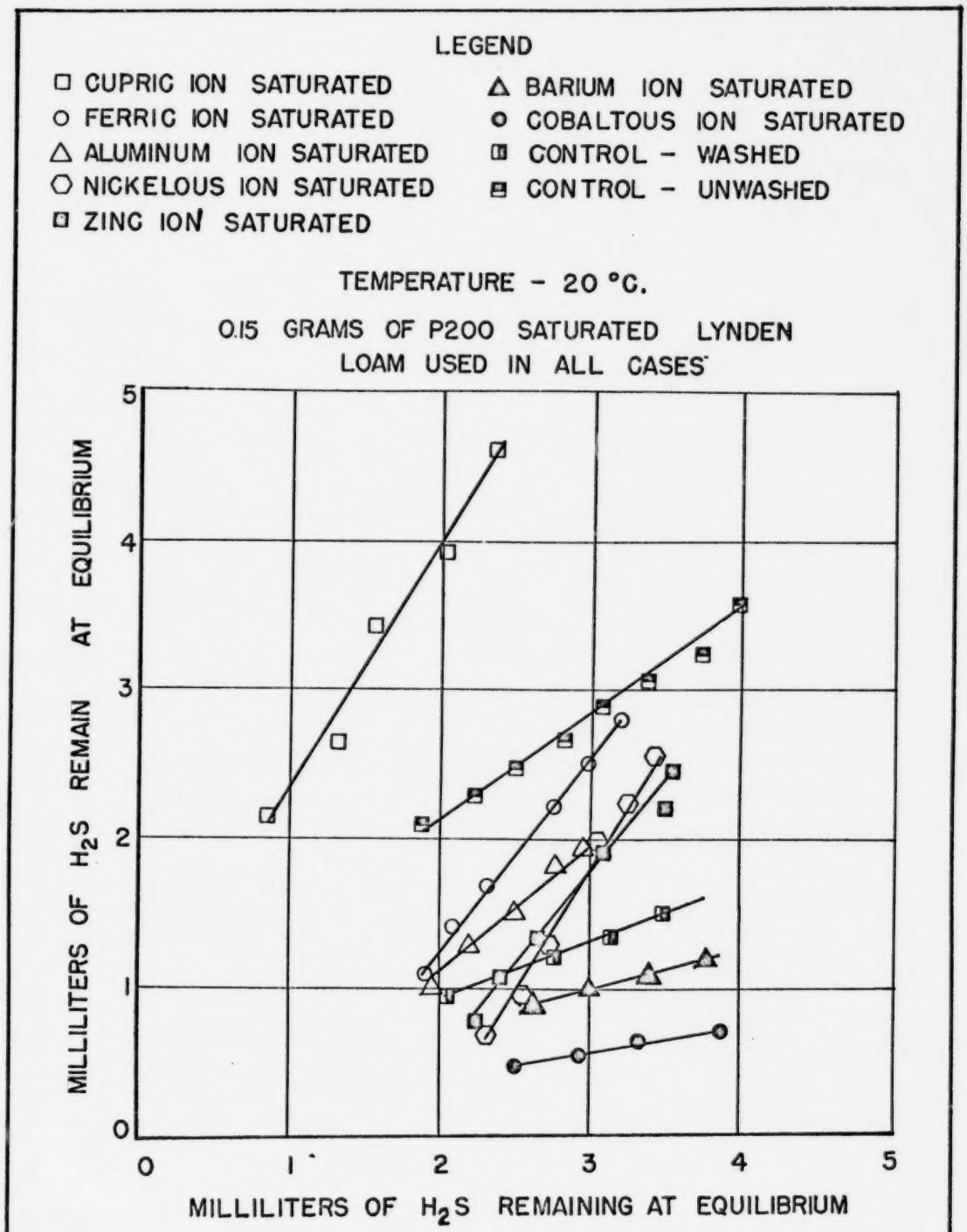


FIGURE 14 - CATION INFLUENCE ON HYDROGEN SULFIDE REMOVAL IN GAS-SOIL SYSTEMS

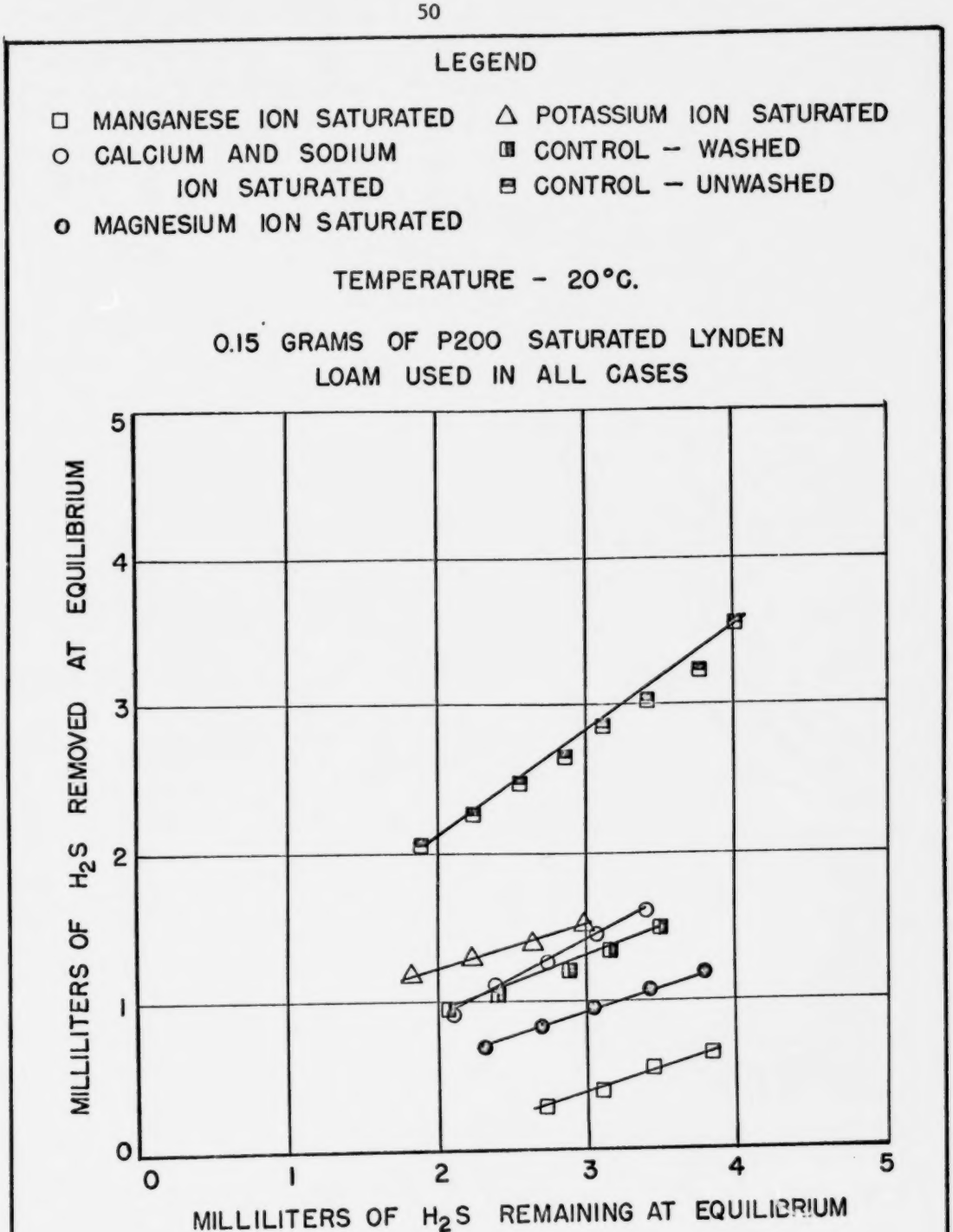


FIGURE 15 - CATION INFLUENCE ON HYDROGEN SULFIDE REMOVAL IN GAS-SOIL SYSTEMS

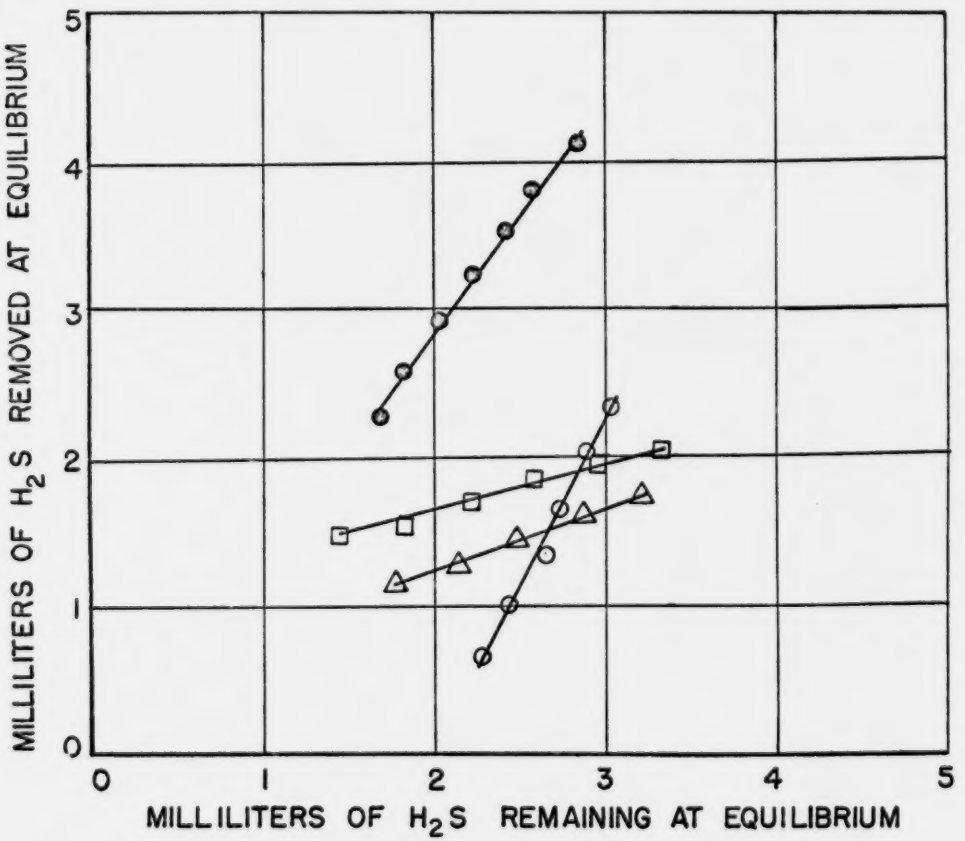


FIGURE 16 – HYDROGEN SULFIDE REMOVAL ISOTHERMS FOR SEVERAL SOILS IN GAS – SOIL SYSTEMS

C. Surface Area Measurements

The surface areas of all soil fractions in relation to liquid-soil and gas-soil uptake isotherms were measured using the modified ethelyene glycol monoethyl ether (EGME) as previously discussed (25). Results of these measurements are shown in Table IV.

Table IV: SOIL SURFACE AREAS

Soil	Surface Area - square meters / gram of soil
P60-R140 Lynden loam	12.40
P140-R200 Lynden loam	15.15
P200 Lynden loam	31.8
P200 Sand	14.6
P200 Clay	32.2
P200 Humus	84.4

D. EDTA Removal From Solution

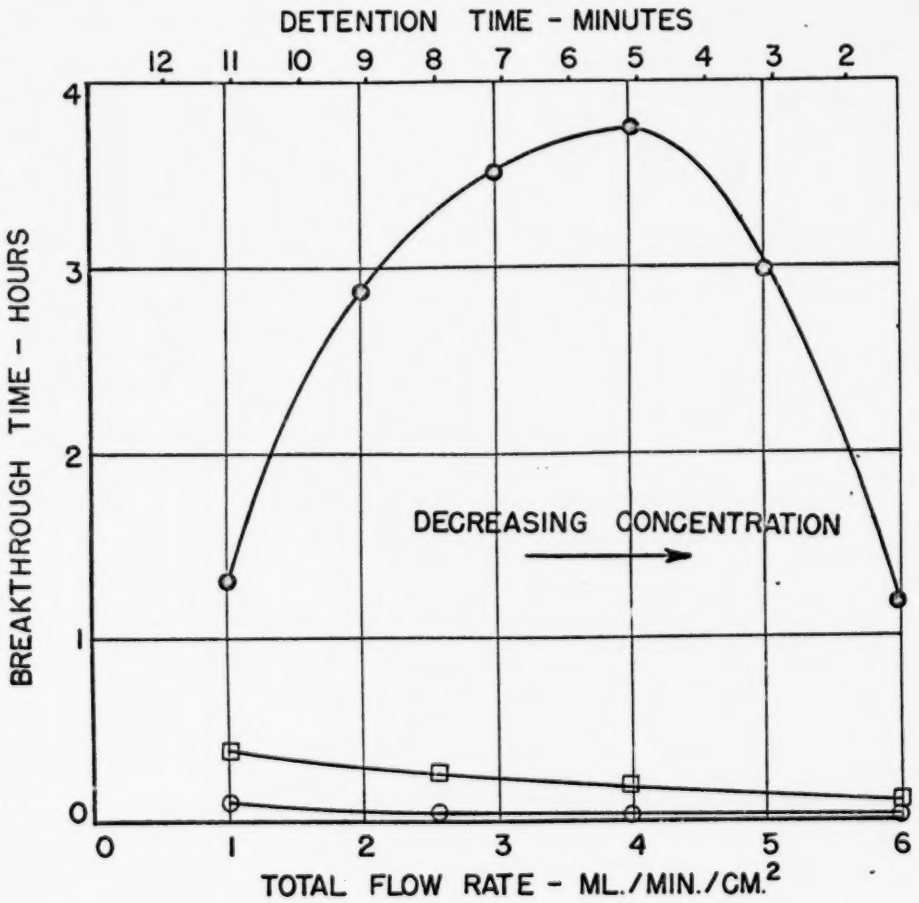
The ability of sterile soil to remove Ethylenediaminetetracetic Acid (EDTA) from a buffered liquid solution was investigated as previously described. The maximum uptake of EDTA at pH 5.8 by the soils previously used in liquid-soil and gas-soil uptake experiments is shown in Table V.

Table V: EDTA UPTAKE BY VARIOUS SOILS

Soil	EDTA Uptake at Equilibrium - $\frac{\text{milligrams}}{\text{gram of soil}}$
P60-R140 Lynden loam	74.4
P140-R200 Lynden loam	81.9
P200 Lynden loam	108.
P200 Sand	79.5
P200 Clay	105.6
P200 Humus	54.6

E. Dynamic Uptake of Hydrogen Sulfide from Air Streams

Using the plastic columns described previously, the ability of the passing number 10 sieve fraction of sterile Lynden loam to remove hydrogen sulfide from moving air streams was investigated. Figure 17 depicts the hydrogen sulfide breakthrough time for dry, sterile soil samples as the total flow rate increased and the hydrogen sulfide flow rate remained constant. Note that concentration decreases from left to right. The upper curve illustrates the results obtained using air as the carrier gas, while the middle curve shows the results with nitrogen used as the carrier vehicle. The lower curve represents calculated values of hydrogen sulfide breakthrough time, assuming no interaction occurring between the gas stream and the soil, and also that "plug-flow" exists at all times. Appearing in Appendix E are the calculations for this curve. In Figure 18, iso-concentration lines are shown on a plot of initial hydrogen sulfide breakthrough time versus total flow rate for previously unused dry, sterile soil samples.

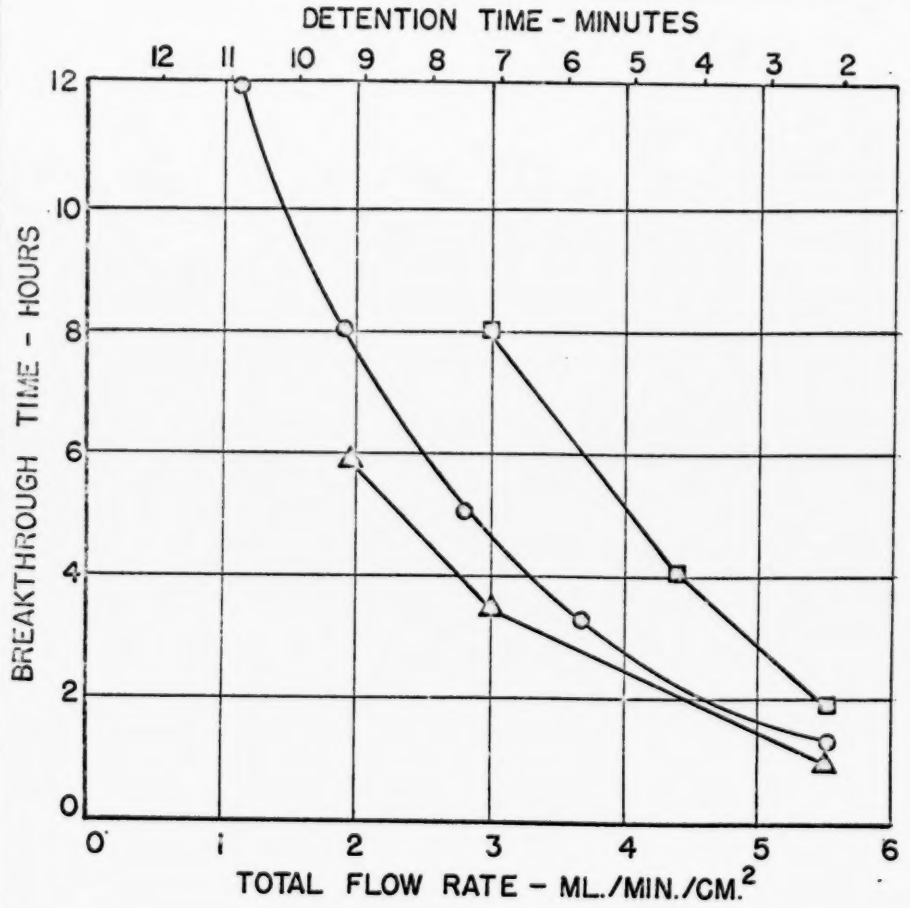

DETENTION TIME - MINUTES
12 11 10 9 8 7 6 5 4 3 2
BREAKTHROUGH TIME - HOURS
0 1 2 3 4
DECREASING CONCENTRATION
0 1 2 3 4 5 6
TOTAL FLOW RATE - ML./MIN./CM.2

LEGEND

- ○ AIR AS CARRIER GAS
- □ NITROGEN AS CARRIER GAS
- ○ CALCULATED CURVE ASSUMING NO INTERACTION BETWEEN SOIL AND H_2S

H_2S FLOW RATE – 10 ML./MIN.
TEMPERATURE – 25°C.
300 GRAMS OF DRY, STERILE, PIO LYNDEN LOAM USED IN EACH CASE

FIGURE 17 – H_2S BREAKTHROUGH TIME VERSUS TOTAL FLOW AT A CONSTANT H_2S FLOW RATE



LEGEND

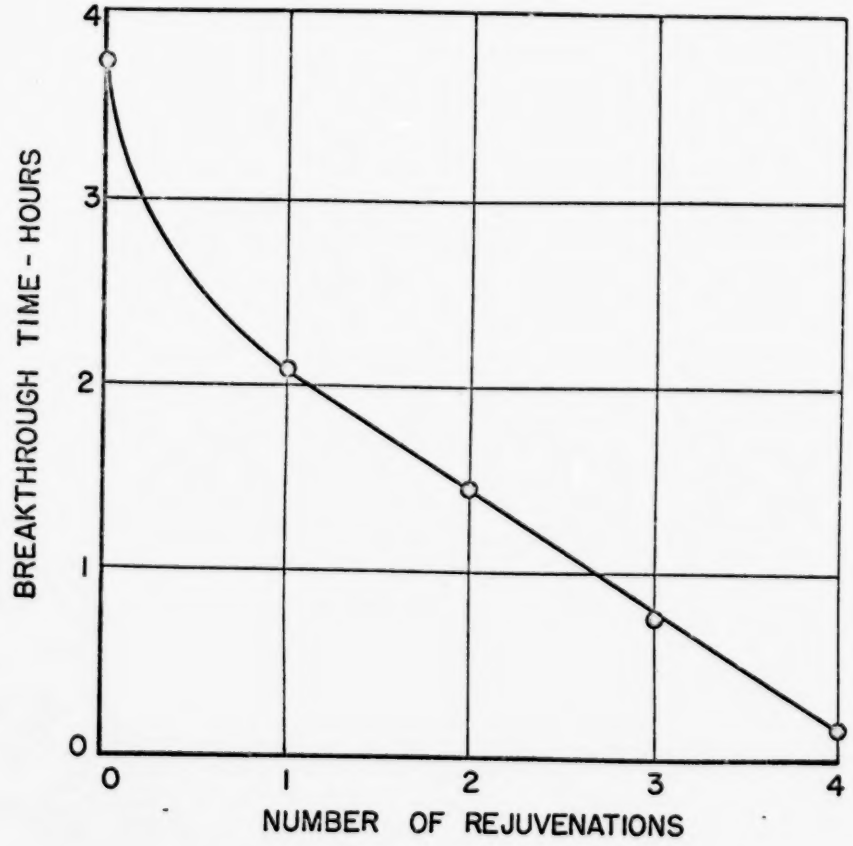
○ 6.6% H_2S INFLUENT CONCENTRATION
□ 10 % H_2S INFLUENT CONCENTRATION
△ 13.3% H_2S INFLUENT CONCENTRATION

AIR CARRIER
TEMPERATURE – 25°C.
300 GRAMS OF DRY, STERILE, P10 LYNDEN LOAM USED IN EACH CASE

FIGURE 18 – H_2S BREAKTHROUGH TIME VERSUS TOTAL FLOW AT FIXED H_2S CONCENTRATIONS

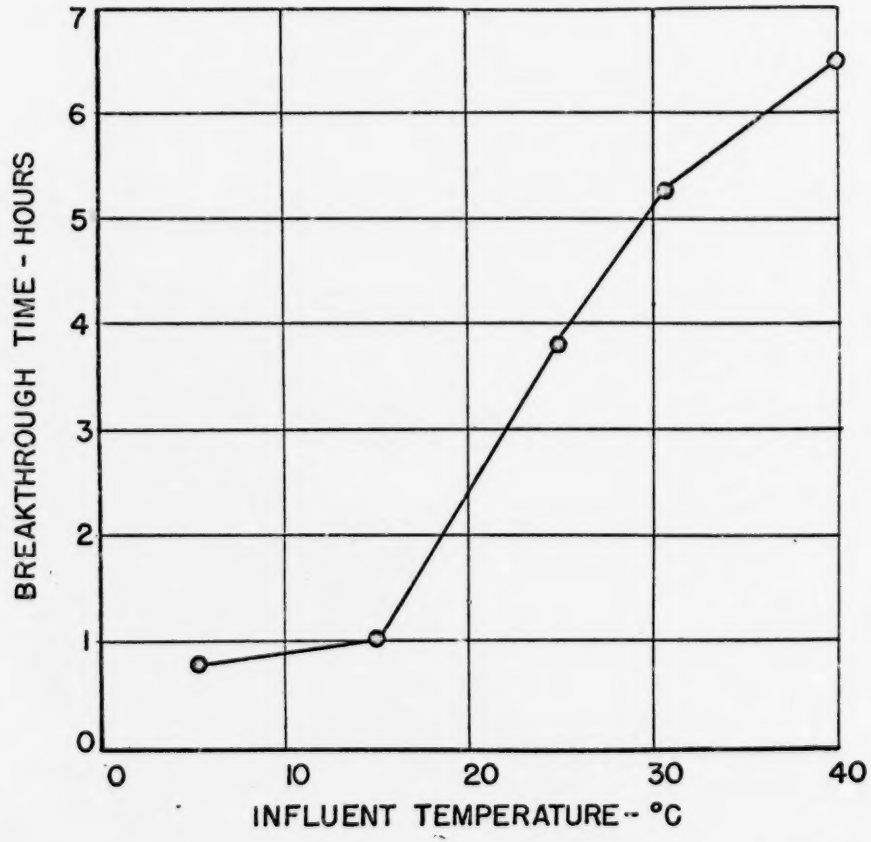
The foregoing two figures represented only the time until initial breakthrough, the soil being disposed of after initial breakthrough. This work was complemented by a series of experiments undertaken to determine what effect the number of rejuvenations had upon hydrogen sulfide breakthrough time. These results are shown in Figure 19 as a plot of hydrogen sulfide breakthrough time versus the number of rejuvenations.

In Figure 20, the influence of influent gas temperature upon initial hydrogen sulfide breakthrough time may be observed. In addition to the previous experiments using dry soils, the influence of soil moisture content upon hydrogen sulfide breakthrough time was also investigated. These results may be seen in Figure 21.



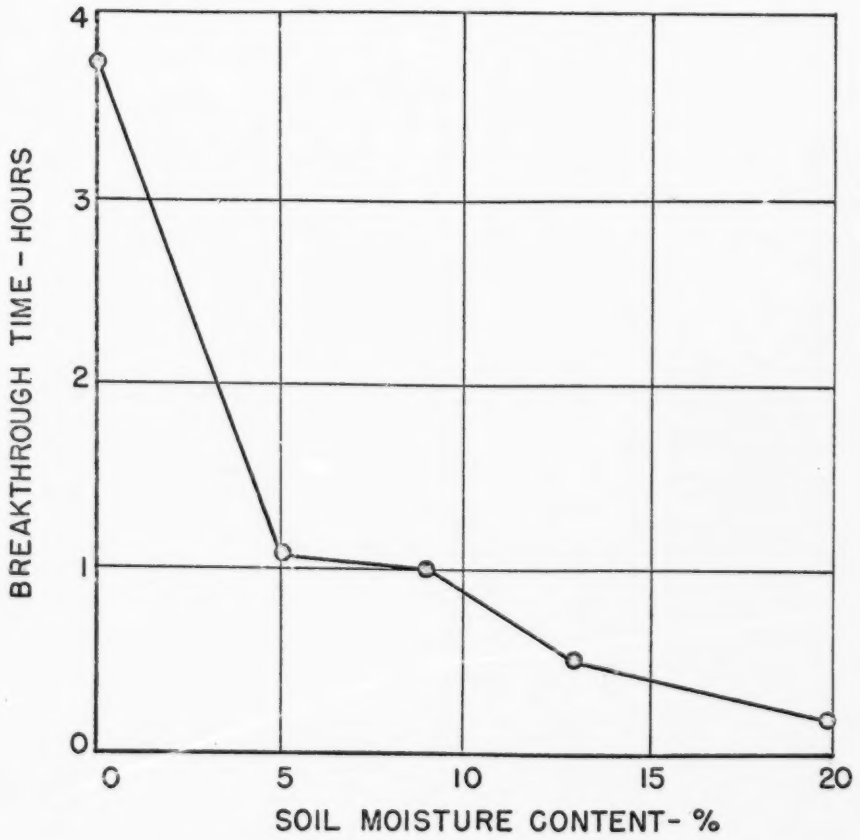
TOTAL FLOW - 3.91 ML./MIN/CM.^{2}
H_2S FLOW - 10 ML./MIN.
DETENTION TIME - 2.92 MIN.
TEMPERATURE - 25°C.
300 GRAMS OF DRY, STERILE, P10 LYNDEN LOAM USED IN EACH CASE

FIGURE 19 - H_2S BREAKTHROUGH TIME VERSUS NUMBER OF REJUVENATIONS



TOTAL FLOW - 3.91 ML./MIN./CM.^{2}
H_2S FLOW – 10 ML./MIN.
DETENTION TIME – 2.92 MIN.
TEMPERATURE – 25°C.
300 GRAMS OF DRY, STERILE, P10 LYNDEN LOAM USED IN EACH CASE

FIGURE 20 - EFFECT OF INFLUENT TEMPERATURE ON INITIAL BREAKTHROUGH TIME



TOTAL FLOW - 3.91 ML./MIN./CM.^{2}
H_2S FLOW - 10 ML./MIN.
DETENTION TIME - 2.92 MIN.
TEMPERATURE - 25°C.
300 GRAMS OF DRY, STERILE, P10 LYNDEN LOAM USED IN EACH CASE

FIGURE 21 - SOIL MOISTURE CONTENT INFLUENCE ON INITIAL H_2S BREAKTHROUGH TIME

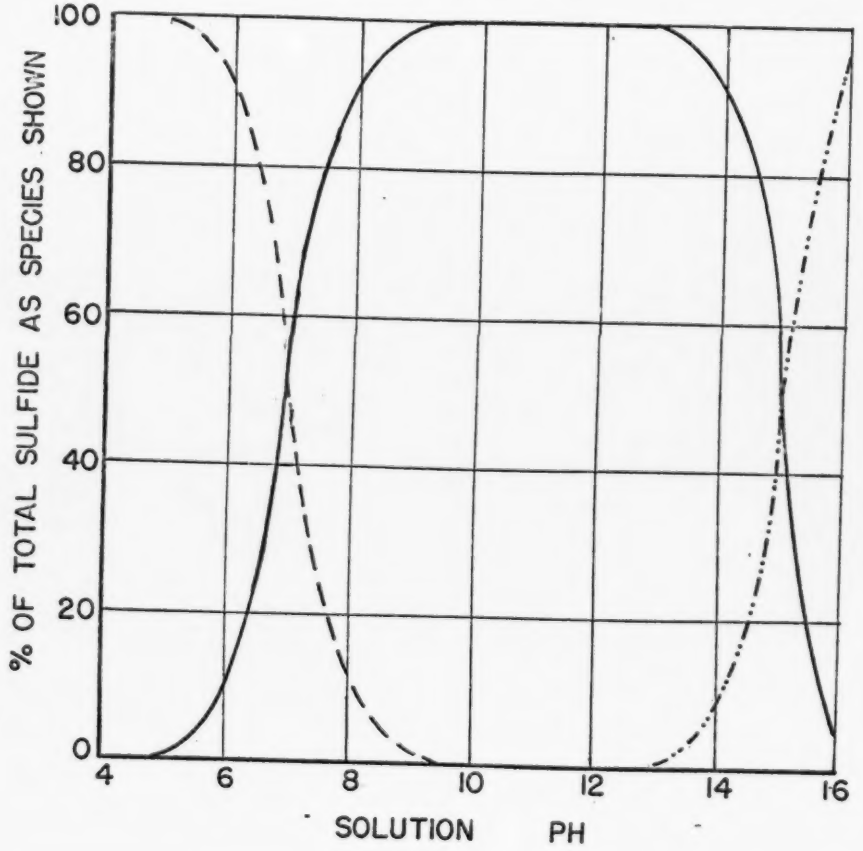
VI. DISCUSSION

A. Influence of Moisture Upon the Removal Mechanism in Batch Scale Testing

Batch scale experimentation has been conducted using both wet and dry soils. In referring to this testing, systems using wet, sterile soil were denoted as liquid soil systems and those using dry, sterile soil as gas-soil systems. It should be noted that different sulfide species were present in the liquid-soil and gas-soil systems. As shown in Figure 22, aqueous hydrogen sulfide, hydrosulfide ion, or sulfide ion may be the predominant species in liquid-soil systems, the predominant species depending on the solution pH. In gas-soil systems, hydrogen sulfide gas was the only sulfide species present.

Changes in temperature produced opposite effects upon the equilibrium removal capacity in liquid-soil and gas-soil systems. At both pH 5.8 and 8.0 in liquid-soil systems, increasing temperatures exerted an increase in the equilibrium removal capacity as shown in Figure 3. Therefore, the sulfide removal mechanism in liquid-soil systems is endothermic. Conversely, as shown by Figure 10, gas-soil systems removed less hydrogen sulfide at equilibrium as temperatures increased. Gas-soil removal systems are therefore exothermic. On the basis of these observed results, different sulfide removal mechanisms are evident in wet and dry soil.

In the liquid-soil uptake studies, soil pH was varied by using three different pH buffering systems. The natural pH of the Lynden loam tested was 5.8. Uptake data was collected at pH values of 4.0, 5.8, and 8.0, Figure 2. This data shows that approximately equal removal occurs at pH 4.0 and 5.8, but also that much better removal occurs at pH 8.0. Either or both of two factors may have been responsible for this increase in sulfide removal ability at pH 8.0. (a) The predominant sulfide species present depends upon solution pH, as shown in Figure 22. At pH 5.8, aqueous hydrogen sulfide



LEGEND

---- $H_2S_{AQUEOUS}$

—— HYDROSULFIDE ION

-·-·- SULFIDE ION

$H_2S \rightleftharpoons HS^- + H^+$ $K_1 = 9.1 \times 10^{-8}$

$HS^- \rightleftharpoons S^= + H^+$ $K_2 = 1.2 \times 10^{-15}$

FIGURE 22 - CALCULATED CURVES OF SOLUTION PH INFLUENCE ON SULFIDE SPECIES PRESENT

accounts for 90% of the total sulfur. Such changes in the predominant sulfur species present could be responsible for the variation in soil equilibrium removal capacity. (b) Changes in the ionization status of soil functional groups may also be responsible for the variation of removal capacity with pH. A change such as this in the ratio of attractive to repulsive forces could change the soil surface area through alteration of the physical structure of the soil.

Although the experimental evidence does not yield a definitive explanation for the better removal experienced in pH 8.0 liquid-soil systems, operation of a field scale installation using Lynden loam would be greatly enhanced at this pH. One method of operating at a pH different from the natural soil pH would be to buffer the soil at the desired pH. This would be extremely advantageous in small scale installations where infrequent maintenance is highly desirable. Another possibility would be intermittent spraying of a basic pH solution over the soil filter installation. This could possibly be practical for a large installation where a source of basic waste water is available, such as that resulting from the sodium hydroxide peeling of potatoes. The feasibility of this idea would have to be determined by further laboratory studies. An alternative possibility where a basic pH waste source is not available would be the use of alkaline soils. Although past research (4) has shown that hydrogen sulfide removal by moist soil results in a decrease of soil pH, it is not possible at this time to determine the effectiveness of moist, alkaline soils for hydrogen sulfide removal.

B. Influence of Moisture upon Dynamic Removal Situations

Because distinctly different mechanisms were found to be operative in moist and dry soils, the effect of moisture upon dynamic removal situations was studied. As shown in Figure 21, decreasing soil service times resulted from increasing soil moisture content. This decrease in breakthrough time may be attributed to any or a combination of several interdependent factors. (a) The ultimate capacity of a moist soil is less than that of a dry soil. (b) The rate of the removal mechanism in a moist soil is less than the removal rate in a dry soil. (c) Blockage of some of the soil interstices may have resulted from water addition. Regardless of the exact reason, it should be quite obvious that wherever possible, soil filters designed to remove hydrogen sulfide should be kept as dry as possible at all times.

Since dry soil evidenced better dynamic removal than moist soil it was felt unnecessary to further investigate the removal ability of moist soils. Therefore, all further dynamic studies utilized air dry soil. It should be noted that water vapor was a by-product of the removal reaction, although air passing through the soil removed this water, leaving the soil dry at all times.

C. Soil Rejuvenation in Dry Dynamic Removal Situations

All dynamic removal studies to this point were concerned solely with the time required for initial breakthrough of hydrogen sulfide, because this is the point normally necessitating filter replacement or rejuvenation. Therefore, the revivification capacity of the soil and conditions essential for revivification were the next aspects to be taken under consideration.

In Figure 17, the influence of the carrier gas upon removal is portrayed. This figure was obtained by maintaining a constant hydrogen sulfide flow, while the total flow through the column varied. As shown,

use of an air carrier produced much longer soil service times than did a nitrogen carrier, other conditions remaining equal. To determine whether use of the nitrogen carrier made the removal mechanism completely inoperative, calculations were made to determine the initial breakthrough time assuming no interaction between the hydrogen sulfide and the soil, Appendix E. Table VI compares these calculated breakthrough times with those observed using nitrogen and air carriers, Figure 17.

Table VI: BREAKTHROUGH TIMES, OBSERVED AND CALCULATED, FOR A 10% H_2S CONCENTRATION

Total - ml/min/cm^2	Breakthrough Time - Hours		
	Calculated Assuming no interaction with the soil	Nitrogen	Air
0.98	0.195	0.44	1.30
1.95	0.097	0.32	2.95
2.93	0.065	0.27	3.50
3.90	0.049	0.24	3.66
4.88	0.039	0.21	2.90
5.86	0.032	0.18	1.66

It is evident from this table that using a nitrogen carrier did not completely inhibit the removal of hydrogen sulfide, but the table also illustrates that using an air carrier gave much larger breakthrough times than did the nitrogen carrier. For example, at a total flow rate of 3.90-ml/min/cm^2 the breakthrough time using a nitrogen carrier was nearly five times longer than the calculated time assuming no interaction with the soil, but the breakthrough time using an air carrier was over fifteen times longer than when using the nitrogen carrier. Therefore, that use of a nitrogen

carrier does not completely inhibit the total removal mechanism should be evident, but it should also be recognized that the presence of air definitely enhances the removal capacity of the soil.

The data presented in Table VI indicates that two operative removal mechanisms comprise the total removal system. The difference between the breakthrough times calculated assuming no interaction of hydrogen sulfide with the soil and the breakthrough times observed using a nitrogen carrier illustrate the effect produced by the first portion of the removal reaction. This first portion of the total reaction will be referred to as the "sulfidation" reaction, a term frequently used to describe the conversion of iron oxide to iron sulfide during the removal of sulfur compounds for natural gas (20). The term sulfidation is only used at this time to refer to the first portion of the removal mechanism and is not meant to imply that iron oxides in the soil are the agents responsible for hydrogen sulfide removal. This initial reaction is followed by a rejuvenation reaction, which may be considered as an oxidation. This oxidation is responsible for the larger breakthrough times observed using an air rather than a nitrogen carrier. In summary, use of a nitrogen carrier allows only the sulfidation reaction to proceed, while use of an air carrier allows both the sulfidation and oxidation reactions to occur concurrently, resulting in more efficient soil utilization.

In the previously discussed testing, it was not known whether the rates of sulfidation and oxidation were equal to each other. To obtain this information, a 10% hydrogen sulfide mixture with an air carrier was passed through a column of dry soil until breakthrough, followed by removal of the soil from the column and exposure to room temperature air overnight. The following morning, the soil was repacked in the column and run again until breakthrough. The process continued until the breakthrough time experienced

was 15 minutes. As shown in Figure 19, the breakthrough time of 15 minutes occurred after four rejuvenations of the soil. This behavior indicates that the rate of sulfidation is more rapid than the oxidation reaction at an H_2S concentration of 10%.

D. Removal of Sulfide from Liquid-Soil Systems

In the removal of sulfide from liquid-soil systems, it was necessary to determine initially the extent of removal which could be attributed to ion exchange. To investigate this possibility, chloride ions were exchanged for the exchangeable anions by shaking Lynden loam overnight in a 10% NaCl solution. The following morning, the liquid was decanted and the soil then washed three times with distilled water to remove any "free" ions. This washed soil was mixed with sodium sulfide and de-oxygenated pH 5.8 buffer, and then allowed to reach equilibrium with respect to sulfide removal. At this equilibrium point, no chloride ions were present in the liquid. Because no chloride ions were released during the sulfide removal, it is evident that the contribution of ion exchange in liquid-soil uptake is negligible.

It was also felt desirable to determine whether removal in liquid-soil systems could be the result of leaching of cations from the soil, followed by reaction of these leached cations with sulfide to form a precipitate. To ascertain this, a sample of Lynden loam was shaken overnight with pH 5.8 buffer. The next morning, the buffer and soil were separated, followed by one washing of the soil with distilled water. Uptake of sulfide at pH 5.8 was conducted on the washed soil and also on a liquid mixture consisting of the originally decanted buffer and the one distilled water washing. Results showed that this pre-treated soil removed exactly the same amount of sulfide as did a soil receiving no pre-treatment, but the system containing the decanted buffer and the distilled water washing removed no sulfide. Therefore,

it is evident that removal of sulfide in liquid-soil systems occurs as the result of interaction with the soil, rather than reaction with leached cations.

When the results of the liquid-soil uptake data were plotted according to the Langmuir and Freundlich isotherm models, Figures 8 and 9, linear relationships were in evidence. Confirmation of these models reinforces the hypothesis that removal occurs at the soil surface, although not necessarily proving the hypothesis. It should be noted that no oxygen was present in the system during these uptake experiments, and therefore no rejuvenation of the soil by oxygen occurred.

Early experimentation with the addition of EDTA to a liquid-soil system indicated that removal of sulfide by wet soil could be completely inhibited by EDTA addition. This indicated the possible existence of a correlation between the maximum uptake capacity of EDTA by soil and the relative sulfide removal capacity. As shown in Table VII, the soils tested are listed in order of their decreasing ability to remove sulfide at pH 5.8. The relative order of removal ability holds through the range of sulfide concentrations studied, Figures 4 and 7. The table illustrates the absence of any relationship between maximum EDTA uptake capacity or EDTA uptake per square meter of surface and the sulfide removal ability. The most probable explanation for this behavior may be attributed to the ability of EDTA to chelate, to some extent, all cations (31). In other words, EDTA chelates both cations associated with sulfide removal and those having no effect upon sulfide removal, therefore EDTA uptake results are not correlatable with sulfide removal.

The linear relationships obtained in plotting the Freundlich and Langmuir isotherm models, Figures 8 and 9, further the hypothesis that removal of

Table VII: SUMMARY OF SOIL PROPERTIES IN LIQUID-SOIL SYSTEMS

Soil Property	Lynden loam P200	Humus P200	Lynden loam P140 - R200	Lynden loam P60 - R140	Sand P200	Clay P200
mg.Sulfide removed / gram of soil at an equil.conc. of 15 mg.l	16.2	15.4	10.4	7.8	7.3	4.0
%Fe	7.471	1.142	7.551	5.90	7.65	11.704
%Cu	0.0058	0.056	0.0044	0.0041	0.0053	0.0434
%Zn	0.0055	0.0154	0.0055	0.0055	0.0064	0.0130
%Pb	Trace	Trace	Trace	Trace	Trace	Trace
%Mn	0.0562	0.104	0.0613	0.0591	0.0641	0.0883
%Mg	0.827	0.072	0.928	0.938	1.019	2.349
%Ca	1.44	0.566	1.579	2.079	1.898	2.503
%Na	1.13	0.1789	1.48	1.62	1.57	2.503
%K	0.654	0.223	0.619	0.704	0.694	1.44
%Al	8.04	1.21	8.09	7.30	7.10	9.52
Σ elements analyzed - %	18.33	3.57	20.32	18.61	20.10	29.34
% Si, O, H, C, and trace	65.17	16.04	70.63	73.89	72.11	67.19
soil surface area (m^2/gram)	31.8	84.4	15.15	12.4	14.6	32.2
maximum EDTA uptake at pH 5.8 (mg/gram)	108	54.6	81.9	74.4	79.5	105.6
EDTA uptake / surface area (mg/m^2)	3.4	0.64	5.4	6.0	5.45	3.28
% volatile	16.5	80.4	9.35	7.5	7.79	3.57

Note: All percentage values are weight %.

sulfide in liquid-soil systems occurs at the soil surface. Therefore, it was felt that a relationship might exist between soil surface area and the ability of the soil to remove sulfide from solution. But as shown in Table VII, no such relationship exists. For example, the clay studied had a relatively large surface area, 32 square meters per gram, but removed less sulfide than any of the other soils tested. Table VII also shows the elemental composition of the soils studied. Correlations were attempted for each soil between the relative ability to remove sulfide from solution and the following: individual elements in the soil, groups of elements such as the heavy metals, alkali metals, and the alkali earth metals, and soil volatile matter. No correlations were found between these factors and the relative sulfide removal ability.

The scope of this research was intentionally restricted to several easily measured parameters in the endeavor to establish a simple correlation factor between the sulfide removal capacity of wet soils. The three factors which were considered are (a) soil surface area, (b) maximum EDTA uptake capacity, and (c) total soil composition. As previous discussions have shown, none of these factors correlated with removal ability, but isotherm evidence suggests that the removal mechanism is a surface phenomena. If such a removal mechanism does exist, a factor which must be considered in addition to surface area is the surface chemical composition. Due to the nonhomogeniety of most soil structures, the surface chemical composition could not be expected to agree with the bulk chemical composition. Unfortunately, measurements of soil surface composition involve highly sophisticated instruments and techniques, placing their utilization outside the simple guidelines considered in this research for soil comparisions.

Because elemental analysis gave no indication of which elements were most desirable at the surface for sulfide removal, twelve cation saturated soils were prepared as previously described. Each of these twelve soils had the exchangeable cations replaced by a known, but in each case different cation. It was felt that the relative removal ability exhibited by these twelve prepared soils could suggest the cations most and least desirable at the soil surface. As Figures 5 and 6 show, the relative removal ability of these twelve soils with respect to the replacing cation was Cu^{+2}, Fe^{+3}, Zn^{+2}, Ni^{+2}, Al^{+3}, Co^{+2}, Mg^{+2}, Mn^{+2}, Ca^{+}, Na^{+}, K^{+}, and Ba^{+2}. It should be mentioned that only the most oxidized form of each element was used in these saturation studies. From the standpoint of overall improvement in soil removal capacity Cu^{+2}, Fe^{+3}, Zn^{+2}, and Ni^{+2} appear to be those cations most desirable at the soil surface. Unfortunately, analysis of the total soil chemical composition yields no indication of the percentage of these elements available at the soil surface.

In summary, the easily measured parameters which were initially selected to relate the sulfide removal capability of wet soils produced no meaningful results. But, uptake tests using soils with known cations replacing the exchangeable cations at the soil surface indicate that Cu^{+2}, Fe^{+3}, Zn^{+2}, and Ni^{+2} are the elements most desirable at the soil surface. At the current time, it is felt that the easiest available method to determine the sulfide removal ability of wet soils is to run a batch uptake test similar to that described within this research.

E. Hydrogen Sulfide Removal in Static Gas-Soil Systems

Static gas-soil testing used either of four gases in combination with hydrogen sulfide. These gases were air, oxygen, carbon dioxide, and nitrogen. As portrayed in Figure 12, use of air or oxygen produced identical hydrogen sulfide removals, while tests using nitrogen or carbon dioxide gave removal identical to each other, but substantially lower removal than oxygen or air. This behavior points out the importance of oxygen, or the oxygen component of air, in rejuvenation of the soil. In fact, the difference between the amount of removal with oxygen present and without oxygen present indicates the extent of rejuvenation at the temperature and concentration under study. For example, Figure 12 shows that P200 Lynden loam at 20°C and an equilibrium hydrogen sulfide concentration of 4500 ppm was rejuvenated approximately two and one-half times.

Any relationship between hydrogen sulfide capacity and the maximum EDTA removal capacity, measured in a liquid-soil system would appear to be invalid due to the rejuvenation ability of the soil, when in contact with oxygen. In other words, although one EDTA molecule may be capable of chelating only one removal "site", this same "site" could take up any number of hydrogen sulfide molecules, depending upon factors to be considered later. In addition, EDTA chelates many different cations (31), some most likely not even responsible for hydrogen sulfide removal. As seen in Table VIII, no relationship exists between the capacity of a soil to remove EDTA from solution and to remove hydrogen sulfide from air.

Table VIII shows the soils studied, listed in order of their decreasing ability to remove hydrogen sulfide, and the elemental composition of these soils. No relationship exists between the ability of these soils to remove hydrogen sulfide and any element, group of similar elements, or the soil

Table VIII: SUMMARY OF SOIL PROPERTIES IN GAS-SOIL SYSTEMS

Soil Property	Clay P200	Lynden loam P200	Lynden loam P140 - R200	Humus P200	Lynden loam P60 - R140
equil. uptake capacity at 5550 ppm mg/gram of soil	181	18.3	12.1	11.3	9.2
%Fe	11.704	7.471	7.551	1.142	5.90
%Cu	0.0434	0.0058	0.0044	0.056	0.0041
%Zn	0.0130	0.0055	0.0055	0.0154	0.0055
%Pb	Trace	Trace	Trace	Trace	Trace
%Mn	0.0883	0.0562	0.0613	0.104	0.591
%Mg	2.349	0.827	0.928	0.072	0.938
%Ca	2.503	1.44	1.579	0.566	2.079
%Na	1.68	1.13	1.48	0.1789	1.62
%K	1.44	0.654	0.619	0.223	0.704
%Al	9.52	8.04	8.09	1.21	7.30
Σ elements analyzed - %	29.34	18.33	20.10	3.57	18.61
% Si, O, H, C, and trace	67.19	65.17	70.63	16.04	73.89
% volatile matter	3.57	16.5	9.35	80.4	7.5
soil surface area (m^2/gram)	32.2	31.8	15.15	84.4	12.4
maximum EDTA uptake at pH 5.8 (mg/gram)	105.6	108	81.9	54.6	74.4
%Fe x surface area	377	236.5	114	96.4	73.2
$\frac{\%Fe \times \text{surface area}}{\text{equil. uptake capacity at 500 ppm}}$	2.08	12.9	9.45	8.51	7.95

Note: All percentage values are weight %.

volatile matter content. However, a relationship does appear between the hydrogen sulfide removal ability and the multiple of soil surface area per gram and the weight percentage of iron in the soil. Comparing this relationship with the hydrogen sulfide equilibrium uptake capacity at 5550 ppm, shown in Table VIII, indicates that the relationship is far from quantitative. In other words, the ratio of $\frac{\%\text{ iron x surface area / gram of soil}}{\text{ML. of } H_2S \text{ removed / gram of soil}}$ is not quantitative, as shown in Table VIII. For example, at an equilibrium concentration of 5550 ppm, P200 clay gave a ratio of 2.08 while P200 Lynden loam gave a ratio of 12.9, in spite of the clay's ability to remove more hydrogen sulfide than Lynden loam. Lack of such a quantitative relationship lends doubt to both the validity and practicality of comparing soils in this manner. Another factor which casts doubt upon this relationship is the requirement that the soil elemental composition remain homogenous throughout the soil structure. This is highly doubtful in soils such as clay and humus, which are negatively charged and surrounded by a layer of charge neutralizing cations.

As previously noted, the Freundlich isotherm model normally best describes multilayer adsorption, whereas the Langmuir model was derived assuming monolayer adsorption upon a surface of identical removal sites. In the uptake of hydrogen sulfide by chemisorption, with rejuvenation of the removal "sites" by oxidation, removal could be pictured as similar to multilayer adsorption, even though the soil surface is not covered. As seen in Figure 12, plotting the observed results according to the Freundlich model yields a linear relationship over the range of concentrations studied. Conversely, the Langmuir model, Figure 13, does not yield a linear relationship for the same data. This behavior appears to indicate that a possible multilayer buildup of sulfur atoms is deposited adjacent to the removal site.

As previously explained when discussing liquid-soil removal, it was felt that running a series of tests using different soils, each having all exchangeable cations replaced by a known cation, would demonstrate which cations were responsible for hydrogen sulfide removal. As Figures 14 and 15 show, the cations listed in order of their decreasing effectiveness were Cu^{+2}, Fe^{+3}, Zn^{+2}, Ni^{+2}, Al^{+3}, K^{+}, Ca^{+2}, Na^{+}, Mg^{+2}, Ba^{+2}, Mn^{+2} and Co^{+2}. Valences shown are the valence of the cation originally used when replacing the exchangeable cations. The latter six of these either only slightly improved the soil's capacity for hydrogen sulfide, or even slightly decreased it, in relation to the "washed" control.

On the basis of the results observed, the ability of the soil to be rejuvenated is readily observable. It also appears evident that oxygen is the gaseous agent responsible for this rejuvenation. Therefore, a mechanism as shown below appears to be responsible for the sulfidation phase of the removal mechanism

$$MO_x + XH_2S \longrightarrow MS_x + XH_2O$$

where M is the cation responsible for the existence of the removal "site". Once this reaction has proceeded, the presence of oxygen in the gas phase oxidizes this sulfided "site". This oxidation reaction may be visualized as

$$2MS_x + XO_2 \longrightarrow 2MO_x + \text{SULFUR}$$

At this point, the "site" has been rejuvenated one time and is available for further sulfidation. Such sulfidation and oxidation reactions proceed continually at each "site" contacted by hydrogen sulfide and oxygen, the overall reaction rate depending upon hydrogen sulfide concentration, reaction zone temperature, and soil moisture; while the total capacity depends upon the soil's capacity to accept the deposited sulfur. Rather than being simply a chemisorption reaction, a more appropriate definition would be contact or surface catalysis, consisting of a sulfidation and oxidation reaction.

A sulfur mass balance was conducted for a soil column containing 300 grams of dry soil operated under the following conditions: inflow temperature - 25°C, H_2S concentration - 10%, total flow rate - 100 ml/min, and an air carrier. Breakthrough time for this column was 3.66 hours, calculations showing that by the time breakthrough occurred 3.06 grams of H_2S had entered, or 0.0102 grams of sulfur per gram of soil. An extraction of sulfur from a uniform mixture of soil gave 0.0100 grams of sulfur per gram of soil. A test was conducted for sulfate ion in this same soil, but none was present. This sulfur mass balance closes within 2.0% between calculated figures and the observed data.

F. The Suggested Method of Design Optimization

The information gathered in the dynamic uptake phase of this research was intentionally limited in the range of concentrations and soil depths studied. This limitation was necessary, since the purpose of the research was the establishment of a method of design optimization and a study of revivification ability, rather than a solution to the design for a particular situation. Therefore, it is not suggested that the results obtained in this limited study should be used directly for application to a field scale installation. Rather, it is suggested that a bench scale study utilizing the actual, or a synthesized air stream to be purified be used for a similar method of data collection and presentation in order to follow the recommended procedure for design optimization.

To operate soil filters removing H_2S from air streams in the most economical fashion, a method of design optimization must be developed to utilize the removal capacity of a soil in the most efficient manner. As Figure 19 illustrates, soil possesses a revivification ability, although breakthrough times are successively shorter as the number of rejuvenations

increases. This shortening of breakthrough time indicates the existence of a maximum soil removal capacity. The most efficient mode of operation would therefore be directed toward achieving a minimum "down time" for soil rejuvenation. To achieve this minimum "down time," the total flow rate per square foot of surface which yields the maximum removal of H_2S prior to breakthrough should be selected. Operation in this manner will allow optimum time utilization of all facilities involved in the operation, such as land, labor, soil holding chambers, pumps, and electrical power.

Before presenting the method of design optimization, a brief discussion of the relevant factors in dynamic removal systems and their inter-relationships will be discussed. Five principal factors influence dynamic removal: (a) detention time, (b) reaction temperature, (c) quantity of hydrogen sulfide entering, (d) initial hydrogen sulfide concentration, and (e) total flow rate per square foot of soil surface. The first three of these will be discussed in the following paragraphs in terms of the latter two and other pertinent factors.

(a) Detention time - Detention time within a soil filter must be sufficiently long to permit all of the hydrogen sulfide to contact a removal site, and also long enough to prevent channeling through the soil. Detention time per unit depth is a function of the total flow rate per square foot of surface and the soil voids ratio.

(b) Reaction temperature - Significance of the reaction temperature is readily portrayed by Figure 20. Although the reaction with dry soil is exothermic (see temperature data in Appendix J) the reaction rate increases with increasing temperature, therefore enhancing the removal efficiency of the soil prior to breakthrough. The reaction temperature is dependent upon the ambient temperature, the total flow rate per square foot, and the amount of hydrogen

sulfide entering per unit time.

(c) Quantity of H_2S Entering per Unit Time - At any concentration, the reaction temperature increases as the amount of hydrogen sulfide entering increases, as shown by the temperature data in Appendix J. The quantity of hydrogen sulfide entering is a function of H_2S influent concentration and the total flow rate per square foot of soil surface.

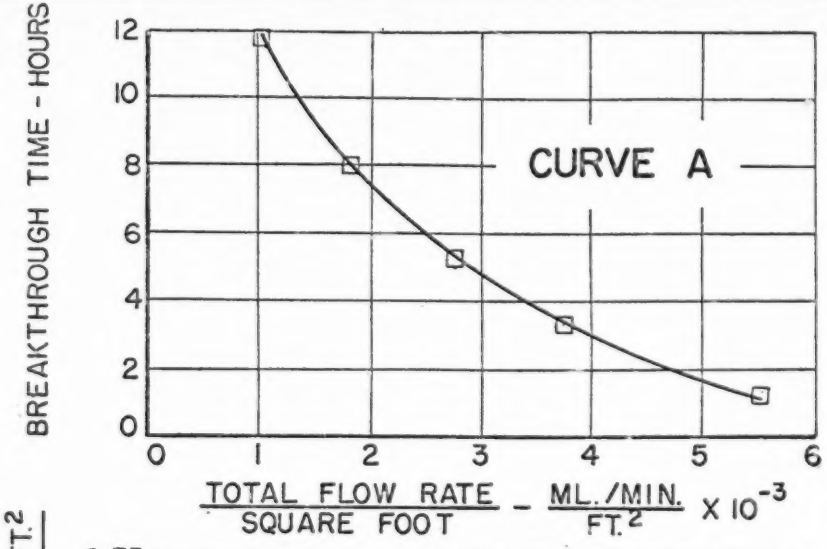
The first step in the design process involves obtaining from bench scale studies a curve of breakthrough time versus the total flow rate per square foot of surface for the gas stream to be purified. It is recommended that the depth of soil utilized in this bench scale testing be the maximum possible available for the full scale installation. This allows for a maximum amount of upward travel of the removal zone prior to breakthrough.

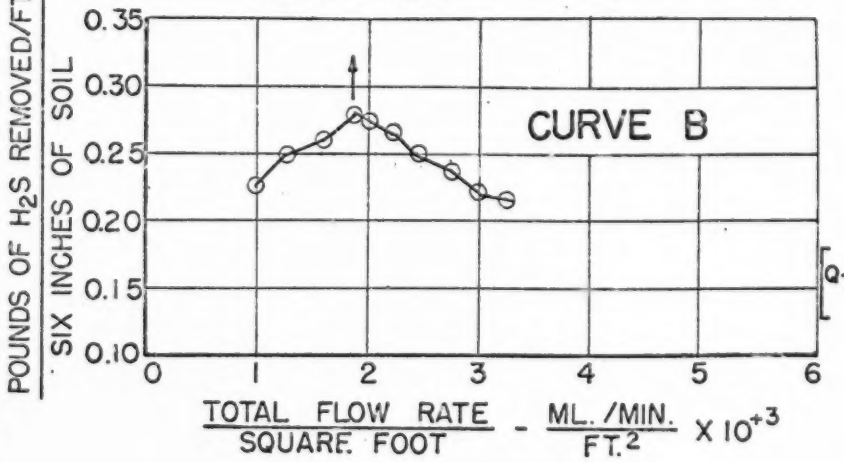
The upper curve (Curve A) of Figure 23 illustrates such a plot of breakthrough time versus total flow rate per square foot of soil surface, obtained from data presented in Figure 16 for a six inch soil depth. Using information from Curve A, a plot (Curve B) of weight of hydrogen sulfide removed per six inch soil depth versus total flow rate per square foot should be plotted directly below. For an example of this calculation, consider the flow of 1750 ml/min/ft^2 which yielded a breakthrough time of 8.4 hours. Therefore:

$$\frac{\text{lb. } H_2S \text{ removed/ft}^2}{\text{6 inches of soil}} = (1750 \text{ ml/min/ft}^2)(0.1 \frac{\text{ml } H_2S}{\text{ml total}})(60 \text{ min/hr})(8.4 \text{ hr})$$
$$(0.307 \times 10^{-5} \frac{\text{lb. } H_2S}{\text{ml } H_2S})$$

$$\frac{\text{lb. } H_2S \text{ removed/ft}^2}{\text{6 inches of soil}} = 0.279 \text{ lb.}$$

Using Curve B, the optimum total flow rate per square foot is conveniently chosen as the flow rate yielding the maximum pounds of hydrogen sulfide removed prior to breakthrough. Using this flow rate per square foot, the number of square feet of surface required at the depth tested can be calculated by dividing the total flow rate of the gas stream to be purified by the optimum flow rate per square foot chosen in the design study.





CONDITIONS FOR CURVE A

TEMPERATURE - 25°C.
H_2S CONCENTRATION - 10%
300 GRAMS OF DRY, STERILE, P 10 LYNDEN LOAM USED IN EACH CASE

POINTS FOR CURVE B WERE OBTAINED USING THE EQUATION:

$$\frac{\text{POUNDS OF } H_2S \text{ REMOVED/FT.}^2}{\text{SIX INCHES OF SOIL}} = \left[Q_{TOTAL}\right]\left[\frac{H_2S \text{ CONC.}}{100}\right]\left[60\frac{\text{MIN.}}{\text{HR.}}\right]\left[3.07 \times 10^{-6}\frac{\text{LB. } H_2S}{\text{ML. } H_2S}\right]\left[\text{BREAK. TIME}\right]$$

FIGURE 23 - METHOD OF DESIGN OPTIMIZATION

VII. SUMMARY

A. Mechanisms

On the basis of the data herein presented, it is possible to postulate mechanisms which describe the removal of S(II) species on soil in both wet and dry conditions.

Wet Soil Removal Mechanism

Removal of sulfide from solution by soil is an endothermic process. Ion exchange is not a factor in removal, moreover agreement of experimental data with the Freundlich and Langmuir isotherms suggest that adsorption is the responsible removal mechanism. Better removals were obtained at pH 8.0 than at pH 4.0 or 5.8, suggesting that hydrosulfide ion and not H_2S (aq) is the active species. Removal is enhanced by the presence of certain cationic species at the soil surface (Cu^{+2}, Fe^{+3}, Zn^{+2}, Ni^{+2}).

Dry Soil Removal Mechanism

Removal of high concentrations of hydrogen sulfide gas by dry soil is a two stage process which is best defined as surface catalysis. Initially hydrogen sulfide reacts with a removal site, according to

$$MO_x + XH_2S \longrightarrow MS_x + XH_2O$$

where MO_x is the cation oxide present at the removal site. In the presence of oxygen, the site is rejuvenated as shown

$$2MS_x + XH_2O \longrightarrow 2MO_x + \text{SULFUR}$$

It is believed that the limitation on the number of possible rejuvenations is due to steric hinderance caused by the deposition of sulfur at the removal site. The cations most desirable at the soil surface are Cu^{+2}, Fe^{+3}, Zn^{+2} and Ni^{+2}.

B. Dynamic Removal Optimization

Removal of high concentrations of hydrogen sulfide from moving air streams is performed much more efficiently by dry soil than wet soil. Inter-related parameters which influence the removal of hydrogen sulfide by dry sterile soil are detention time, reaction temperature, amount of hydrogen sulfide entering, concentration of hydrogen sulfide, and the total flow rate. A method of design optimization is presented (Figure 23) which determines for a given concentration and influent gas temperature, the total flow rate at which the maximum removal of hydrogen sulfide per unit time results. It is felt that this design optimization method should be restricted to air streams containing only hydrogen sulfide, until further research delineates the removal mechanism for other odorous gases.

VIII. REFERENCES

1. Matheson Gas Data Book, Furnished by the Matheson Company, Inc., Newark, California (1965).

2. Summer, W., Methods of Air Deodorization, Elsevier Publishing Co., London (1963).

3. Pomeroy, R. D., "Deodorization of Gas Streams by the Use of Microbiological Growths," U. S. Patent Office, No. 2, 793,096 (1967).

4. Gumerman, R. C., "Preliminary Experimentation on the Removal of High Concentrations of Hydrogen Sulfide by Soil," Typewritten Manuscript, University of Washington (1966).

5. Mayo, R., "Mercer Island Sewer District Odor Control Study," Unpublished Report, Seattle, Washington (1962).

6. Carlson, D. A. and Leiser, C. P., "Soil Beds for the Control of Sewage Odors," Journal Water Pollution Control Federation, 38, 829 (May, 1966).

7. Leiser, C. P., Typewritten Master's Degree Thesis, University of Washington, Seattle, Washington (1964).

8. Gregg, S. J., The Surface Chemistry of Solids, Reinhold Publishing Corporation, New York (1961).

9. Brey, W. S., Principles of Physical Chemistry, Appleton-Century-Crofts, Inc., New York (1958).

10. Brunauer,S., The Adsorption of Gases and Vapors, Princeton University Press (1943).

11. Barrow, G. M., Physical Chemistry, McGraw-Hill Book Company, Inc., New York (1961).

12. Den Besten, I. E. and Selwood, P. W., "The Chemisorption of Hydrogen Sulfide, Methyl Sulfide, and Cyclohexane on supported Nickel Catalysts," Journal of Catalysis, 1, 93 (1962).

13. Roberts, M. W. and Ross, J. R. H., "Kinetics of the Dissociation of Hydrogen Sulfide by Iron Films," Transactions Faraday Society, 2301-2308, (1966).

14. Siedlewski, J., "Mechanisms of Catalytic Oxidation on Activated Carbon, VIII. Oxidation of Hydrogen Sulfide," Roczniki Chem., 4C, 87-100 (1966).

15. Foust, A. S., et al., Principles of Unit Operations, John Wiley and Sons, New York (1960).

16. Bear, F. E. - Editor, Chemistry of the Soil, Reinhold Publishing Corporation, New York (1964).

17. Grim, R. E., Clay Mineralogy, McGraw-Hill Book Company, Inc., New York (1953).

18. Dean, L. A. and Rubins, E. J., "Anion Exchange in Soils: 1. Exchangeable Phosphorous and the Anion-Exchange Capacity," Soil Science, 63, 377 (1947).

19. Grant, R. J., "The Adsorption of Hydrogen Sulfide by Copper and Copper-Iron Impregnated Carbons," Unpublished Report, Pittsburgh, Pennsylvania (December 20, 1960).

20. Nonhebel, G. - Editor, Gas Purification Processes, George Newnes Limited, London (1964).

21. Griffith, R. H. and Morcom, A. R., "The Interconversion of Iron Oxides and Sulfides," Journal of the Chemical Society, 14, 786 (1945).

22. Jacobs, M. B., Braverman, M. M., and Hocheiser, S., "Ultramicrodetermination of Sulfides in Air," Analytical Chemistry, 29, 1349 (1957).

23. Jacobs, M. B., The Chemical Analysis of Air Pollutants, Interscience Publishers, Inc., New York (1960).

24. Standard Methods for the Examination of Water and Wastewater, Eleventh Edition, American Public Health Association, Inc., New York (1960).

25. Heilman, M. D., Carter, D. L., and Gonzalez, C. L., "The Ethylene Glycol Monoethyl Ether (EGME) Technique for Determining Soil-Surface Area," Soil Science, 100, 409 (1965).

26. McNeal, B. L., "Effect of Exchangeable Cations on Glycol Retention by Clay Minerals," Soil Science, 97, 96 (1964).

27. Simon, R. H. and Schollenberger, C. J., "The Acetone Method of Extracting Sulfur from Soil," Soil Science, 20, 393 (1925).

28. Jackson, M. L., Soil Chemical Analysis, Prentice-Hall Inc., Englewood Cliffs, N. J. (1964).

29. ASTM Committee D-18, Procedures for Testing Soils, American Society for Testing Materials, Philadelphia, Pa. (1958).

30. Lange, N. A. - Editor, Handbook of Chemistry, Handbook Publishers, Inc., Sandusky, Ohio (1949).

31. Ringbom, A., Complexation in Analytical Chemistry, Interscience Publishers, Inc., New York (1963).

IX. APPENDICES

APPENDIX A

HENRY'S LAW CONSTANTS FOR HYDROGEN SULFIDE IN DISTILLED WATER (15)

Temperature - °C	Henry's Law Constant - Atm./Mole Fraction
0	$2.68 \times 10^{+2}$
10	$3.67 \times 10^{+2}$
20	$4.83 \times 10^{+2}$
30	$6.09 \times 10^{+2}$
40	$7.45 \times 10^{+2}$
50	$8.84 \times 10^{+2}$
60	$1.03 \times 10^{+3}$
70	$1.19 \times 10^{+3}$
80	$1.35 \times 10^{+3}$
90	$1.44 \times 10^{+3}$

APPENDIX B

EXAMPLE CALCULATION OF HYDROGEN SULFIDE SOLUBILITY IN DISTILLED WATER

Conditions: 0°C water exposed to pure hydrogen sulfide gas at 1 Atmosphere Pressure.

$$X = \frac{P_{H_2S}}{H} = \frac{1 \text{ atm.}}{0.268 \times 10^{+4} \text{ atm/mole frac.}} = 37.4 \times 10^{-4} \text{ mole fractions}$$

For 100 gms of water,

$$N_{H_2O} = \frac{100}{18} = 5.56 \text{ gram moles}$$

$$\therefore \quad N_{H_2S} = (37.4 \times 10^{-4})(5.56 \text{ gm moles}) = 208 \times 10^{-4} \text{ gm moles}$$

at 0°C 1 gm mole H_2S = 22.4 liters

$$\frac{\text{ml } H_2S \text{ dissolved}}{100 \text{ gms of water}} = (\text{gm moles } H_2S)\left(\frac{\text{liters } H_2S}{\text{gm mole}}\right)\left(\frac{\text{ml}}{\text{liter}}\right)$$

$$= (2.08 \times 10^{-2} \text{ gm moles})(22.4 \text{ liters/gm mole})(10^3 \text{ ml/liter})$$

$$= 466 \text{ ml } H_2S/100 \text{ ml water}$$

APPENDIX C

COMPOSITION OF BUFFER MIXTURES

pH 3.8

1.94 milliliters concentrated hydrochloric acid

91.909 grams of potassium biphthalate

Enough distilled water to yield 9 liters total volume

pH 5.8

15.474 grams of sodium hydroxide

91.909 grams of potassium biphthalate

Enough distilled water to yield 9 liters total volume

pH 8.0

17.648 grams of sodium hydroxide

61.241 grams of monopotassium phosphate

Enough distilled water to give 9 liters total volume

APPENDIX D

EFFECTIVE IONIC RADII OF SELECTED CATIONS (30)

Ion	Ionic Radius - Angstron Units
Al^{+++}	0.57
Ba^{++}	1.43
Ca^{++}	1.06
Co^{++}	0.82
Cu^{++}	1.0
Fe^{+++}	0.67
K^{+}	1.33
Mg^{++}	0.78
Mn^{++}	0.91
Na^{+}	0.98
Ni^{++}	0.78
Zn^{++}	0.83

APPENDIX E

CALCULATIONS FOR BREAKTHROUGH TIME ASSUMING NO INTERACTION WITH THE SOIL

$$\text{Volume of column occupied by Raschig Rings} = \frac{\pi D^2 h}{4} = \frac{\pi(2.25 \text{ in.})^2(2 \text{ in.})}{4}$$

$$= 7.96 \text{ in}^3 = \frac{7.96 \text{ in}^3}{0.062 \text{ in}^3/\text{cm}^3}$$

$$= 128.5 \text{ cm}^3$$

Volume of Raschig Rings = 55 cm^3

Hence, void volume in the lower portion of the column

$$= 128.5 \text{ cm}^3 - 55 \text{ cm}^3$$

$$= 73.5 \text{ cm}^3$$

$$\text{Volume of column occupied by soil} = \frac{\pi D^2 h}{4} = \frac{\pi(2.25 \text{ in})^2(6 \text{ in})}{4}$$

$$= 23.9 \text{ in}^3 = \frac{23.9 \text{ in}^3}{0.062 \text{ in}^3/\text{cm}^3} = 386 \text{ cm}^3$$

From Appendix I, the voids ratio of the soil = 0.56, Hence,

$$0.56 = \frac{\text{volume of voids}}{\text{total volume}}$$

$$0.56 = \frac{\text{void volume}}{386 \text{ cm}^3}$$

$$\text{void volume} = 219 \text{ cm}^3$$

$$\text{Therefore, time to breakthrough} = \frac{\text{total void volume}}{Q \text{ total}}$$

$$= \frac{73.5 \text{ cm}^3 + 219 \text{ cm}^3}{Q \text{ total}}$$

$$= \frac{292 \text{ cm}^3}{Q \text{ total}}$$

Using this formula, the following table was calculated:

Q_{Total} - ml/min	Q_{Total} - ml/min/cm^2	Breakthrough Time - minutes
25	0.975	11.7
62.5	2.44	4.67
100	3.91	2.92
150	5.86	1.95

APPENDIX F

LIQUID-SOIL UPTAKE TESTS - LYNDEN LOAM

Soil Condition	C initial mg/l	C Equil. mg/l	mg/l Removed	X-mg	X/M- mg/gm	C Equil. / X/M
P200,20°C,pH 5.8	9.6	2.4	7.2	2.16	2.16	1.11
	18.4	7.2	11.2	3.36	3.36	2.14
	36.2	18.4	17.8	5.34	5.34	3.34
	36.8	18.4	18.4	5.52	5.52	3.33
P200,20°C,pH 4.0	7.32	0.48	6.84	2.05	2.05	0.23
	25.2	11.4	13.8	4.14	4.14	2.75
	25.2	11.8	13.4	4.02	4.02	2.93
	35.8	18.4	17.4	5.22	5.22	3.33
P200,20°C,pH 8.0	9.28	3.04	6.24	1.87	1.87	1.62
	19.0	4.8	14.2	4.26	4.26	1.12
	28.3	7.35	21.65	6.50	6.50	1.13
	29.0	8.0	21.0	6.30	6.30	1.26
P200,5°C,pH 5.8	8.8	2.56	6.24	1.87	1.87	1.37
	8.8	3.04	5.76	1.73	1.73	1.75
	24.8	14.1	10.7	3.21	3.21	4.39
	25.4	14.7	10.7	3.21	3.21	4.58
	32.8	20.7	12.1	3.63	3.63	5.70
	32.8	20.2	12.6	3.78	3.78	5.35
P200,45°C,pH 8.0	9.31	1.5	7.81	2.60	2.60	0.576
	18.8	3.0	15.8	5.26	5.26	0.570
	28.2	4.4	23.8	7.92	7.92	0.555
	37.4	5.9	31.5	10.5	10.5	0.561

LIQUID-SOIL UPTAKE TESTS - LYNDEN LOAM

Soil Condition	C initial mg/l	C Equil. mg/l	mg/l Removed	X-mg	X/M- mg/gm	C Equil. X/M
P200,45°C,pH 5.8	8.65	1.28	7.47	2.24	2.24	0.57
	18.9	4.15	14.75	4.43	4.43	0.94
	26.5	7.35	19.15	5.75	5.75	1.28
	35.0	9.75	25.25	7.58	7.58	1.29
P140-R200,20°C, pH 5.8	9.3	1.92	7.4	2.22	2.22	0.865
	9.75	1.92	7.9	2.37	2.37	0.810
	22.4	13.0	9.4	2.82	2.82	4.60
	23.2	13.0	10.2	3.06	3.06	4.25
	30.4	19.2	11.2	3.36	3.36	5.71
	30.4	19.8	10.6	3.18	3.18	6.23
P60-R140,20°C pH 5.8	9.3	1.76	7.54	2.26	2.26	0.78
	9.75	2.40	7.35	2.2	2.2	1.09
	22.4	14.9	7.5	2.25	2.25	6.6
	23.2	14.9	8.3	2.49	2.49	5.97
	30.4	22.4	8.0	2.40	2.40	9.34
P200-Organic Free 20°C, pH 5.8	9.6	2.24	7.36	2.21	2.21	1.01
	18.4	6.4	12.0	3.60	3.60	1.78
	27.2	12.0	15.2	4.56	4.56	2.63
	36.2	15.8	20.4	6.11	6.11	2.58
	36.8	16.5	20.3	6.09	6.09	2.72
P200-Organic Free Control,20°C,pH 5.8	9.75	2.56	7.19	2.15	2.15	1.19
	17.8	9.75	9.45	2.84	2.84	3.43
	19.2	8.95	8.85	2.66	2.66	3.36
	27.4	15.2	12.2	3.66	3.66	4.15

LIQUID-SOIL UPTAKE TESTS - CATION SATURATED LYNDEN LOAM

Soil Condition	C initial mg/l	C Equil. mg/l	mg/l Removed	X-mg	X/M- mg/gm	C Equil. / X/M
Barium ion saturated P200,20°C,pH 5.8	9.75	3.84	5.91	1.77	1.77	2.17
	18.7	10.7	8.0	2.4	2.4	4.45
	18.7	11.4	7.3	2.19	2.19	5.2
	27.4	17.0	10.4	3.11	3.11	5.46
	27.4	16.5	10.9	3.26	3.26	5.05
Cobaltous ion saturated P200,20°C,pH 5.8	8.95	2.56	6.4	1.92	1.92	1.33
	9.75	2.56	7.2	2.16	2.16	1.18
	4.42	8.0	10.7	3.2	3.2	3.34
	27.4	13.4	14.0	4.2	4.2	3.34
	36.5	18.9	17.6	5.26	5.26	3.34
	37.8	19.4	18.4	5.51	5.51	3.37
Aluminum ion saturated P200,20°C,pH 5.8	9.1	2.72	6.38	1.91	1.91	1.42
	14.7	3.84	10.86	3.26	3.26	1.18
	25.2	10.6	13.6	4.07	4.07	2.6
	34.0	17.1	16.9	5.06	5.06	3.38
Washed, P200 20°C,pH 5.8	9.1	2.24	6.86	2.06	2.06	1.09
	14.7	6.1	8.6	2.58	2.58	2.37
	33.4	17.1	16.3	4.88	4.88	3.5
	34.0	17.1	16.9	5.06	5.06	3.34
Cupric ion saturated,P200,20°C,pH 5.8	8.95	1.6	7.35	2.2	2.2	0.73
	9.75	1.6	8.15	2.44	2.44	0.66
	18.7	2.72	16.0	4.8	4.8	0.57
	27.4	4.16	23.2	6.95	6.95	0.6
	36.5	6.09	30.4	9.11	9.11	0.66
	37.8	6.72	31.1	9.3	9.3	0.65

LIQUID-SOIL UPTAKE TESTS - CATION SATURATED LYNDEN LOAM

Soil Condition	C initial mg/l	C Equil. mg/l	mg/l Removed	X-mg	X/M- mg/gm	C Equil. X/M
Ferric ion saturated P200,20°C,pH 5.8	9.45	3.2	6.25	1.87	1.87	1.71
	16.8	4.95	11.85	3.54	3.54	1.4
	25.1	5.75	19.35	5.78	5.78	1.0
	31.7	8.15	23.55	7.05	7.05	1.15
Zinc ion saturated P200 20°C,pH 5.8	9.11	3.04	6.07	1.82	1.82	1.67
	16.6	4.48	12.0	3.6	3.6	1.24
	25.1	6.25	18.85	5.65	5.65	1.11
	31.5	9.0	22.6	6.78	6.78	1.33
Nickelous ion saturated P200,20°C,pH 5.8	9.1	1.44	7.66	2.3	2.3	0.63
	15.8	3.84	12.7	3.82	3.82	1.0
	16.5	3.84	12.0	3.6	3.6	1.07
	23.7	7.35	16.35	4.9	4.9	1.5
	31.5	12.3	19.2	5.75	5.75	2.14
	32.4	12.3	20.1	6.04	6.04	2.04
Calcium ion saturated P200,20°C,pH 5.8	8.8	2.4	6.4	1.92	1.92	1.25
	16.8	5.44	11.36	3.4	3.4	1.6
	25.1	11.3	13.8	4.14	4.14	2.74
	31.7	16.8	14.9	4.46	4.46	3.77
Manganese ion saturated P200,20°C,pH 5.8	9.11	2.72	6.39	1.92	1.92	1.41
	16.5	6.55	9.95	2.99	2.99	2.19
	30.9	16.5	14.4	4.32	4.32	3.82
	31.5	16.5	15.0	4.5	4.5	3.67

LIQUID-SOIL UPTAKE TESTS - CATION SATURATED LYNDEN LOAM

Soil Condition	C initial mg/l	C Equil. mg/l	mg/l Removed	X-mg	X/M- mg/gm	C Equil. X/M
Potassium ion saturated P200,20°C,pH 5.8	6.07	1.28	4.8	1.44	1.44	0.82
	10.4	3.5	6.9	2.07	2.07	1.69
	17.8	8.0	9.8	2.94	2.94	2.72
	26.4	15.2	11.2	3.34	3.34	4.55
Magnesium ion saturated P200,20°C.pH 5.8	6.07	1.6	5.5	1.65	1.65	0.97
	10.4	4.0	6.4	1.92	1.92	2.09
	17.8	8.5	9.3	2.79	2.79	3.05
	26.4	12.65	13.7	4.10	4.10	3.08
Sodium ion saturated P200,20°C,pH 5.8	6.4	1.44	5.0	1.5	1.5	0.96
	13.4	2.4	10.8	3.24	3.24	0.74
	20.3	8.8	11.5	3.45	3.45	2.55
	26.4	13.6	12.8	3.84	3.84	3.54

LIQUID-SOIL UPTAKE TESTS - MISCELLANEOUS SOILS

Soil Condition	C initial mg/l	C Equil. mg/l	mg/l Removed	X-mg	X/M- mg/gm	C Equil. X/M
Humus,P200,20°C pH 5.8	9.3	0.8	8.5	2.55	2.55	0.31
	17.9	5.9	12.0	3.6	3.6	1.64
	26.9	12.5	14.4	4.32	4.32	2.9
	37.3	20.3	17.6	5.28	5.28	3.84
Sand,P200,20°C pH 5.8	9.75	4.0	5.75	1.72	1.72	2.33
	19.2	12.3	6.9	2.07	2.07	5.94
	27.4	19.4	8.0	2.4	2.4	8.09
Clay,P200,20°C pH 5.8	15.7	12.3	3.4	1.02	1.02	12.1
	25.0	20.7	5.3	1.59	1.59	13.0
	33.0	26.7	6.3	1.89	1.89	14.1

APPENDIX G

GAS-SOLID UPTAKE TESTS - LYNDEN LOAM

Soil Condition	Soil wt-gm	ml Injected	ml Remain	ml Remove	X-mg	X/M-mg/gm	C Equil.-ppm	C/X/m
5°C. P200	0.15	7.5	3.03	4.47	6.3	42.0	5610	133
		7.0	2.86	4.14	5.84	38.9	5300	136
		6.5	2.65	3.85	5.42	36.1	4900	136
		6.0	2.45	3.55	5.0	33.3	4540	136
		5.5	2.25	3.25	4.58	30.6	4540	136
		5.0	2.06	2.95	4.16	27.8	3820	137
		4.5	1.85	2.65	3.74	24.9	3420	137.5
		4.0	1.70	2.33	3.28	21.9	3150	144
20°C, P200	0.15	7.5	4.05	3.45	4.86	32.4	7500	231
		7.0	3.78	3.22	4.54	30.3	7000	231
		6.5	3.45	3.05	4.30	28.7	6390	223
		6.0	3.13	2.87	4.05	27.0	5800	215
		5.5	2.86	2.64	3.72	24.8	5300	214
		5.0	2.55	2.45	3.45	23.0	4720	205
		4.5	2.25	2.25	3.17	21.1	4160	198
		4.0	1.93	2.07	2.92	19.4	3580	184
45°C, P200	0.15	7.5	4.75	2.75	3.88	25.8	8800	341
		7.0	4.32	2.68	3.78	25.2	8000	318
		6.5	3.96	2.54	3.68	23.9	7340	307
		6.0	3.61	2.39	3.37	22.5	6690	297
		5.5	3.25	2.25	3.17	21.1	6020	286
		5.0	2.89	2.11	2.98	19.8	5540	278
		4.5	2.52	1.98	2.79	18.6	4660	250
		4.0	2.15	1.85	2.61	17.4	3980	229
20°C, P140-R200	0.15	5.0	3.10	1.90	2.68	17.8	5770	322
		4.5	2.75	1.75	2.47	16.4	5110	311
		4.0	2.50	1.50	2.11	14.1	4630	328
		3.5	2.20	1.30	1.82	12.2	4070	33[illegible]
		3.0	1.90	1.10	1.55	10.3	3520	341
20°C, P60-R140	0.15	5.0	3.41	1.59	2.24	14.9	6310	420
		4.5	3.07	1.43	2.02	13.4	5690	425
		4.0	2.76	1.25	1.75	11.7	5210	447
		3.5	2.40	1.10	1.55	10.3	4440	430
		3.0	1.90	1.00	1.41	9.4	3520	374

GAS-SOLID UPTAKE TESTS - CATION SATURATED LYNDEN LOAM

Soil Condition	Soil wt-gm	ml Injected	ml Remain	ml Remove	X-mg	X/M-mg/gm	C Equil.-ppm	C/X/m
Cupric ion saturated 20°C	0.15	7.0	2.40	4.60	6.48	43.2	4440	103
		6.0	2.08	3.92	5.52	36.8	3850	105
		5.0	1.58	3.42	4.82	32.1	2930	91
		4.0	1.35	2.65	3.74	24.9	2500	100
		3.0	0.85	2.15	3.03	20.2	1575	78
Ferric ion saturated 20°C	0.15	6.0	3.23	2.77	3.90	26.0	5980	230
		5.5	3.01	2.49	3.50	23.3	5580	239
		5.0	2.79	2.21	3.12	20.8	5160	248
		4.0	2.33	1.67	2.35	15.7	4310	275
		3.5	2.10	1.40	1.98	13.2	3890	295
		3.0	1.91	1.09	1.54	10.3	2020	196
Aluminum ion saturated 20°C	0.15	6.0	3.56	2.44	3.44	22.9	6600	288
		5.5	3.32	2.18	3.08	20.5	6150	300
		5.0	3.27	2.23	3.14	20.9	6050	289
		4.0	2.67	1.33	1.87	12.5	4950	396
		3.5	2.43	1.07	1.51	10.1	4670	462
		3.0	2.25	0.75	1.06	7.08	4170	589
Nickelous ion saturated	0.15	6.0	3.45	2.55	3.68	24.5	6400	261
		5.5	3.27	2.23	3.14	20.9	6050	289
		5.0	3.06	1.94	2.73	18.2	5660	311
		4.0	2.67	1.33	1.87	12.5	4950	396
		3.5	2.56	0.94	1.32	8.85	4740	535
		3.0	2.31	0.69	0.97	6.48	4280	660
Zinc ion saturated 20°C	0.15	5.0	3.04	1.96	2.76	18.4	5640	306
		4.5	2.77	1.83	2.58	17.2	5130	298
		4.0	2.50	1.50	2.22	14.1	4640	328
		3.5	2.20	1.30	1.83	12.2	4070	334
		3.0	1.91	1.09	1.53	10.2	3540	347
Washed	0.15	5.0	3.5	1.5	2.22	14.1	6480	460
		4.5	3.15	1.35	1.90	12.7	5840	460
		4.0	2.78	1.22	1.72	11.46	5150	560
		3.5	2.42	1.08	1.52	10.1	4480	444
		3.0	2.05	0.95	1.34	8.95	3800	424

GAS-SOLID UPTAKE TESTS - CATION SATURATED LYNDEN LOAM

Soil Condition	Soil wt-gm	ml Injected	ml Remain	ml Remove	X-mg	X/M-mg/gm	C Equil.-ppm	C/X/m
Cobaltous ion saturated 20°C	0.15	4.5	3.78	0.72	1.015	6.77	7000	1032
		4.0	3.35	0.65	0.92	6.1	6200	1018
		3.5	2.95	0.55	0.775	5.17	5460	1058
		3.0	2.53	0.47	0.662	4.41	4690	1060
Manganese ion saturated 20°C	0.15	4.5	3.84	0.66	0.93	6.2	7110	1148
		4.0	3.45	0.55	0.775	5.17	6400	1238
		3.5	3.10	0.40	0.565	3.77	5740	1525
		3.0	2.72	0.28	0.394	2.63	5040	1910
Calcium ion saturated 20°C	0.15	5.0	3.40	1.60	2.26	15.1	6300	417
		4.5	4.0	1.44	2.03	13.5	5670	420
		4.0	2.74	1.26	1.775	11.85	5070	428
		3.5	2.40	1.10	1.55	10.32	4450	430
		3.0	2.10	0.90	1.27	8.47	3890	459
Sodium ion saturated 2°C	0.15	5.0	3.41	1.59	2.24	14.95	6310	422
		4.5	3.09	1.41	1.985	13.2	5720	434
		4.0	2.77	1.23	1.735	11.56	5130	444
		3.5	2.45	1.05	1.48	9.87	4540	460
		3.0	2.15	0.85	1.20	8.00	3980	497
Potassium ion saturated 20°C	0.15	4.5	2.98	1.52	2.14	14.3	5520	386
		4.0	2.63	1.37	1.93	12.9	4870	378
		3.5	2.21	1.29	1.82	12.2	4100	336
		3.0	1.81	1.19	1.68	11.2	3350	299
Magnesium ion saturated 20°C	0.15	5.0	3.78	1.22	1.72	11.5	7000	609
		4.5	3.41	1.09	1.535	10.25	6310	616
		4.0	3.04	0.96	1.365	9.03	5620	623
		3.5	2.67	0.83	1.17	7.8	4950	635
		3.0	2.30	0.70	0.985	6.55		
Barium ion saturated 20°C	0.15	5.0	3.79	1.21	1.705	11.38	7020	616
		4.5	3.41	1.09	1.537	10.25	6320	616
		4.0	3.02	0.98	1.38	9.2	5590	607
		3.5	2.63	0.87	1.225	8.17	4860	595
		3.0	2.25	0.75	1.058	7.05	4170	592

GAS-SOIL UPTAKE TESTS - LYNDEN LOAM

Soil Condition	Soil wt-gm	ml Injected	ml Remain	ml Remove	X-mg	X/M-mg/gm	C Equil.-ppm	C/X/m
P200, 20°C Carbon Dioxide Atmosphere	0.4	5.0	2.4	2.60	3.66	9.15	4500	491
		4.0	1.65	2.35	3.31	8.27	3060	369
		3.5	1.25	2.25	3.17	7.92	2310	292
		3.0	0.85	2.15	3.03	7.58	1575	208
P200, 20°C Nitrogen Atmosphere	0.4	5.0	2.38	2.62	3.69	9.21	4410	479
		4.5	2.05	2.45	3.45	8.62	3800	451
		4.0	1.68	2.32	3.27	8.18	3110	380
		3.0	0.87	2.13	3.01	7.50	1610	215
P200, 20°C Oxygen Atmosphere	0.15	7.0	3.81	3.19	4.49	30.0	7050	235
		6.0	3.10	2.90	4.08	27.2	5740	211
		5.0	2.53	2.47	3.56	23.7	4690	198
		4.0	1.94	2.06	2.90	19.3	3600	187

GAS-SOLID UPTAKE TESTS - MISCELLANEOUS SOILS

P200 Sand, 20°C	0.15	5.5	3.07	2.43	3.42	22.8	5690	250
		5.0	2.91	2.09	2.94	19.6	5390	275
		4.5	2.76	1.74	2.45	16.35	5110	312
		4.0	2.60	1.40	1.675	13.2	4820	365
		3.5	2.45	1.05	1.48	9.85	4530	460
		3.0	2.31	0.69	0.98	6.47	4280	661
P200 Clay, 20°C	0.02	5.5	3.36	2.14	3.02	151	6220	42.1
		5.0	2.97	2.03	2.86	143	5500	38.4
		4.5	2.61	1.89	2.66	133	4840	36.3
		4.0	2.24	1.76	2.48	124	4150	33.5
		3.5	1.86	1.64	2.31	115	3440	30.0
		3.0	1.46	1.54	2.17	108	2700	25.0
P200 Humus, 20°C	0.15	5.0	3.22	1.78	2.51	16.75	5960	356
		4.5	2.87	1.63	2.30	15.3	5310	348
		4.0	2.51	1.49	2.10	14.0	4650	332
		3.5	2.16	1.34	1.89	12.6	4000	318
		3.0	1.79	1.21	1.705	11.39	3310	291

APPENDIX H

DYNAMIC UPTAKE TESTS USING 300 GRAMS OF THE P. 10 FRACTION OF STERILE LYNDEN LOAM

Inflow Temp.	Total Flow ml/min	Total Flow ml/min/cm^2	H_2S Flow Rate-ml/min	H_2S Conc. -%	Soil Moisture Content - %	Carrier Gas	Prev.No. of Regen-erations	Breakthrough Time - hr	Detention Time - min
25°C	25	0.975	10	40	DRY	AIR	ZERO	1.3	11.7
25°C	50	1.88	10	20	↓	↓	↓	2.95	5.85
25°C	75	2.93	10	13.3				3.50	3.89
25°C	100	3.91	10	10				3.66	2.92
25°C	125	4.88	10	8				2.90	2.33
25°C	150	5.86	10	6.66				1.66	1.95
25°C	25	0.975	10	40	DRY	N_2	ZERO	0.44	11.7
25°C	66.6	2.6	10	15	↓	↓	↓	0.28	4.38
25°C	100	3.91	10	10				0.24	2.92
25°C	150	5.86	10	6.66				0.18	1.95
25°C	75	2.93	5	6.66	DRY	AIR	ZERO	8.0	3.89
25°C	125	4.88	8.33	6.66	↓	↓	↓	4.44	2.33
25°C	50	1.88	6.66	13.3	DRY	AIR	ZERO	5.6	5.85
25°C	100	3.91	10	10	DRY	AIR	1	2.10	2.92
25°C	100	3.91	10	10	↓	↓	2	1.46	2.92
25°C	100	3.91	10	10			3	0.66	2.92
25°C	100	3.91	10	10			4	0.20	2.92
25°C	100	3.91	10	10	5	AIR	ZERO	1.12	2.92
25°C	100	3.91	10	10	9	↓	↓	1.02	2.92
25°C	100	3.91	10	10	13			0.46	2.92
25°C	100	3.91	10	10	19.75			0.16	2.92
5°C	100	3.91	10	10	DRY	AIR	ZERO	0.75	2.92
15°C	100	3.91	10	10	↓	↓	↓	1.04	2.92
40°C	100	3.91	10	10				3.06	2.92
25°C	31	1.21	3.1	10	DRY	AIR	ZERO	11.7	9.42
25°C	74	2.89	7.4	10	↓	↓	↓	5.0	3.95

APPENDIX I

PHYSICAL DESCRIPTION OF LYNDEN LOAM

pH - 5.8

Volatile Matter Content - 7.63

Elemental Sulfur - 0 mg/10 grams of dry soil

Sulfate Ion - 0.33 mg/10 grams of dry soil

Soil Conductance - 2.58×10^{-2} micro

Voids Ratio - 0.56

Liquid Limit - 25

Plasticity Index - N.P.

Sieve Analysis of the Plow Layer

- % Passing No. 4 - 100
- % Passing No. 10 - 99.31
- % Passing No. 20 - 88.54
- % Passing No. 40 - 64.57
- % Passing No. 60 - 41.32
- % Passing No. 140 - 19.35
- % Passing No. 200 - 12.89

APPENDIX J

REACTION ZONE TEMPERATURES IN DYNAMIC UPTAKE TESTS

Total Flow ml/min	Total Flow ml/min/cm^2	Reaction Zone Temperature
36.2	1.41	34°C
72.4	2.82	40°C
108.6	4.23	46°C
144.6	5.64	52°C
181.0	6.05	57°C

Conditions for Testing

H_2S Concentration - 10%

Soil Moisture - Dry

Carrier Gas - Air

Soil - P10 Lynden loam

APPENDIX K

FUTURE WORK

While conducting the research herein, the need for the investigation of some inter-related problems not within the scope of the research was noted. It is suggested that future research be conducted on the topics:

1. Whether sterile soils are as effective as biologically viable soil filters in removing H_2S concentrations below 50 ppm should be investigated.

2. Whether soil filters can effectively remove other malodorous gas such as ethyl mercaptan, indole, and skatole from air streams should be investigated.